

Sorption equilibria and diffusion of toluene, methanol, and cyclohexane in/through elastomers

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ABSTRACT: Molecular transport of toluene, methanol, and cyclohexane and their mixtures in Chemraz 505 elastomer has been investigated using gravimetric techniques for short and long time exposure in these solvents. The sorption–desorption results have been used to calculate the diffusion coefficients by solving Fick's equation under appropriate boundary conditions. The dependence of sorption, desorption, diffusion, and permeation on temperature and composition changes was also studied. The results are discussed in terms of possible interactions between Chemraz 505 polymer and the solvent molecules. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43449.

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INTRODUCTION

Diffusion and permeation of organic solvents in polymeric materials are of high importance in many applications and the object of considerable scientific interest.^{1–4} When a penetrant diffuses into a dry cross linked polymeric network, the polymer chains adopt new configuration in an attempt to accommodate the incoming solvent molecules (i.e., polymer sorption), and the polymer may suffer a swelling process in some extent. When the polymer is in its saturated “swelled” state it has the potential to lose solvent to its surroundings (i.e., polymer desorption), reversing the condition of the polymer to a resemblance of its original dry configuration. The loss of solvent through desorption is not an exact reversal of sorption, owing to the nonlinear structure of polymeric chains and to possible interactions polymer-solvent. Permeation of chemicals within an elastomer may affect the mechanical performance of the material when exposed to aggressive organic chemicals,^{5,6} as in the case of O-rings, a sealing commonly used to avoid or restrict mass leaking. Tests are generally performed by immersing a polymer sample in a pure solvent volume and kept under constant conditions, though real applications of polymeric materials often require contact with solvent mixtures. Permeation of chemicals into the gasket may lead to a displacement due to swelling or yielding to some loss of chemicals (toxic) by permeation. To some extent all polymers are permeable to chemicals;

therefore an evaluation of the diffusivity and permeation of solvents through these materials is essential.

A variety of perfluoroelastomers has been developed for engineering and industrial applications. Chemraz[®] is a trade name of the company Green Tweed; it is a peroxide crosslinked perfluoroelastomer composed by a copolymer of tetrafluoroethylene (TFE) and perfluoromethylvinyl ether (PMVE) and a cure site monomer (CSM), in which all hydrogen atoms have been replaced by fluorine. The chemical structure of the polymeric molecule can be thus represented as $[(CF_2CF_2)_x(CF_2CF(OCF_3))_y]_n$, where x , y , and n stand for the number of units.⁷ It is used to produce special O-rings whose chemical resistance makes them well suited as sealants for a wide range of applications in harsh environments (aerospace, automotive, pollution control, and chemical industries) and in a wide range of temperatures (–30 to 230 °C). Our current interest in examining permeation of ternary mixtures composed by toluene, methanol, and cyclohexane through Chemraz 505 is motivated by the experiment DCMIX (diffusion and thermodiffusion coefficients measurements in mixtures) performed onboard the International Space Station (ISS).^{8–10} In the microgravity experiment diffusion and thermodiffusion coefficients are measured by optical digital interferometry^{11,12} at points of the ternary mixture with specific compositions (points 1–5 in Figure 1).

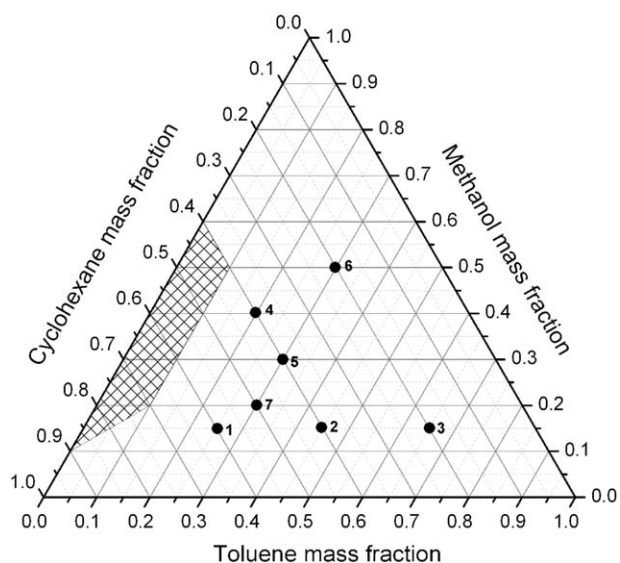


Figure 1. Map of toluene–methanol–cyclohexane in mass fractions (dots show selected 1–5 DCMIX2 points and additional points 6 and 7 complementary mixtures; shaded region outlines demixing zone).

In order to be able to accomplish those measurements the experimental cell⁹ with test liquid must stay bubble free at least during a few months so, preliminary experimental tests at room temperature are done to verify the compatibility between liquids and sealants. For this specific mixture–sealant system QinetiQ Space reported the observation of vapour bubbles and/or demixing of the liquid within the next 67–180 days (Figure 2).^{13,14} This is probably due to permeation of solvents out of the cell, through the gaskets, creating bubbles of vapor.

Results of measurements of sorption and calculated diffusion coefficients are obtained for short time and long time exposure to the liquids.¹⁵ The evolution as a function of time of the soaking of the gaskets is used to achieve a better understanding of the permeability of the Chemraz 505 elastomer to the solvents and to evalu-

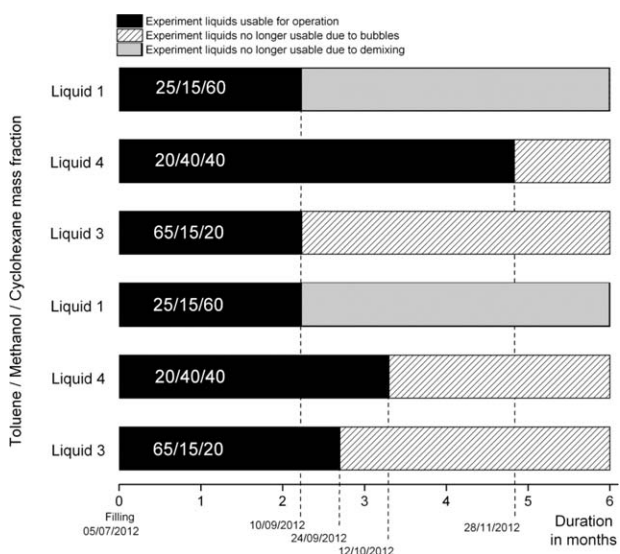


Figure 2. Schematically representation of the in ground test sequence for experimental liquids.^{13,14}

Table I. Composition of the Experimental Liquid Mixtures

Liquid	Toluene	Methanol	Cyclohexane
1	25	15	60
2	45	15	40
3	65	15	20
4	20	40	40
5	30	30	40
6	30	50	20
7	30	20	50

ate the composition of the liquid after formation of small bubble. Using solution–diffusion model¹⁴ the permeation coefficient P is calculated for pure liquids and for mixtures. Since the microgravity experiment was aimed to measure coefficients of thermodiffusion, while applying a temperature difference between opposite sides of cell $\Delta T = 5^\circ\text{C}$, and mean temperature 25°C ,¹⁶ it is important to have two sets of experiments: one at room temperature ($T = 21^\circ\text{C}$) that represents the preliminary ground test, and another at $T = 25^\circ\text{C}$. While comparing results for the two sets of experiments we are able to see variation of parameters over the temperature difference $\Delta T = 5^\circ\text{C}$.

EXPERIMENTAL

The sealing materials used in this work are commercially available under the trade name of Chemraz 505 and were supplied by QinetiQ Space. The reagent grade solvents Toluene 99.85% (CAS Number: 110-82-7) supplied by Acros Organics, Methanol, 99.99% (CAS Number: 67-56-1) and Cyclohexane, 99.99% (CAS Number: 110-82-7) supplied by Fisher Scientific were used without further purification.

Elastomers used in this study had square ring shape with lateral side dimensions of approximately 1.8 mm and thickness 2.052 mm and a specific gravity of 1.93. For sorption measurements, several dry samples of known weight were introduced each in a screw-tight test bottle containing 10 cm^3 of the test solvent (pure solvent or mixture of particular concentration). Table I describes the mixtures used in this study as a function of the mass fraction of toluene (Tol)/methanol (MeOH)/and cyclohexane (CHex). Bottles were stored at atmospheric pressure. A set of samples were placed in a thermostatic bath at $25 (\pm 0.1)^\circ\text{C}$ for temperature control. A second identical set was kept at laboratory temperature at $21 (\pm 1.5)^\circ\text{C}$.

Periodically the immersed samples were removed from the test bottles and the liquid on the surface of the gasket was wiped off with filter paper. The mass of the sample was measured in a Sartorius balance with accuracy of 0.1 mg and then placed back in its test bottle. Time required for this operation was shorter than 30 s therefore errors in weigh due to evaporation of solvents were minimized. Equilibrium sorption was reached in most cases after 10 days.

After completion of sorption runs, samples were placed in a closed ventilated chamber for desorption measurements. Desorption runs were performed by keeping the already saturated samples in a closed chamber at 25°C under atmospheric pressure. The mass loss

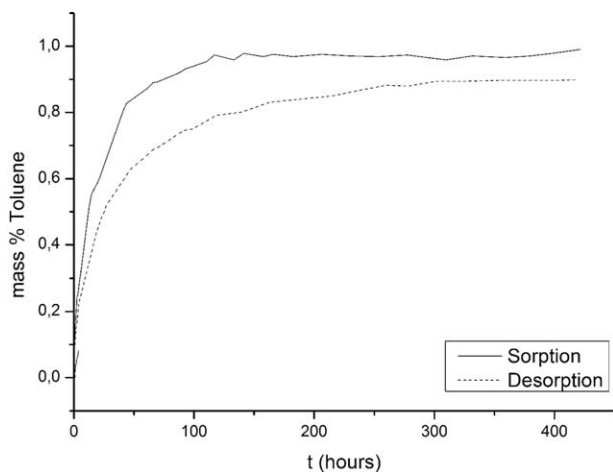


Figure 3. Experimental sorption/desorption curves of toluene in Chemraz 505.

by the samples was monitored at regular intervals of time by removing them from the chamber and weighing in the same manner as was done in sorption experiments. When the samples attained equilibrium sorption or desorption, no more mass gain or loss occurred nor significant changes by keeping the samples inside the containers for a further period of 1 or 2 days. Figure 3 represents a typical sorption and/or desorption experiment for Toluene in Chemraz 505 perfluoroelastomer.

RESULTS AND DISCUSSION

Transport mechanism for liquids inside polymer matrices is important for considerations of their technological applications and is essentially the same for all the permeating molecules.^{1–4,17,18} Diffusion coefficient, D , provides a measure of the rate of diffusion of solvents in the polymer matrices. Fick's second law can be used to estimate the diffusion coefficient¹ from one-dimensional equation for the rate of sorption or desorption of a liquid from a polymer

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial z^2} \right) \quad (1)$$

where C is the concentration and z is the coordinate. If the polymer sample is considered as a long circular cylinder in which diffusion is radial then diffusion equation in cylindrical coordinate system can be solved for concentration-independent diffusivity D in two ways:

before 50–55% sorption^{18,19}

$$\frac{\bar{C}(t)}{C_\infty} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{r^2} \right)^{1/2} \quad (2)$$

after steady sorption is attained

$$\bar{C}(t) = C_\infty \left\{ 1 - \frac{4}{r^2} \sum_{i=0}^{\infty} \frac{1}{\alpha_i^2} \exp[-\alpha_i^2 Dt] \right\} \quad (3)$$

where r is the radius of the cylinder, $\bar{C}(t)$ is the concentration in $\text{cm}^2 \text{ s}^{-1}$ averaged over radius r , t is sorption time, and α_n is the n th root of equation $J_0(\alpha r) = 0$, where J_0 is the Bessel function of averaged the first kind of order zero.

Solving these equations requires some assumptions to be made.²⁰ Samples are considered infinite, i.e., liquid diffusion into the poly-

mer takes place in the x direction only and changes in dimensions are negligible; sorption takes place under transient conditions with a constant diffusivity, and solvent concentration on the membrane surface, during sorption, reaches equilibrium immediately.

To relate the above equations to sorption measurements, mean concentration $C(t)$ can be replaced by quantity of diffusing substance, M_t , which has entered the rubber in time t , and C_∞ by corresponding quantity after infinite time (i.e., equilibrium saturation), M_∞ . Thus, $C(t) \approx M_t$ and $C_\infty \approx M_\infty$.

Sorption Kinetics

Sorption results, s , obtained by exposure of Chemraz 505 to toluene, methanol, cyclohexane, and ternary mixtures of these liquids are calculated from the mass of liquid sorbed per 100 g of the elastomer and expressed in mass percent units. Liquid sorption by the polymer is inferior to 1.1% for pure components and 1.5% for most the mixtures (Figures 4 and 5). The standard deviations in s values are in the range 0.01–0.05.

Analysis of sorption curves before 50–55% sorption can provide relevant information concerning the type of diffusion mechanism. Rearranging eq. (2) one obtain^{14,17}:

$$\frac{M_t}{M_\infty} = Kt^n \quad (4)$$

where the parameter K is a function of polymer type and nature of the solvent molecules, related to both the diffusion parameters and polymer–solvent interactions; and the value of the exponent, n , indicates the type of the transport mechanism. The values of K and n have been calculated using a least squares procedure and are presented in Table II, together with the sorption results.

From analysis of Table II we can see that the data are mostly described by Fickian diffusion (n varies between 0.5 and 0.52).¹⁷ This is also supported from the non sigmoidal nature of the sorption curves shown in Figures 4 and 5. Although these penetrant–polymer systems obey Fickian diffusion and therefore the mobility of the penetrant is much larger than the polymer chain

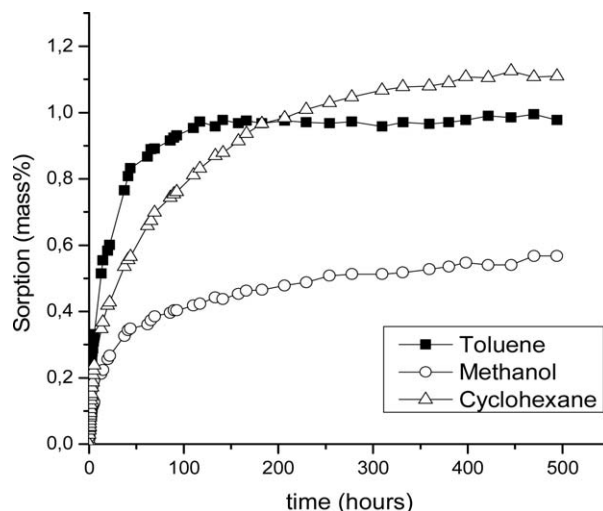


Figure 4. Sorption curves of Chemraz 505 for toluene (■) methanol (○), and cyclohexane (△).

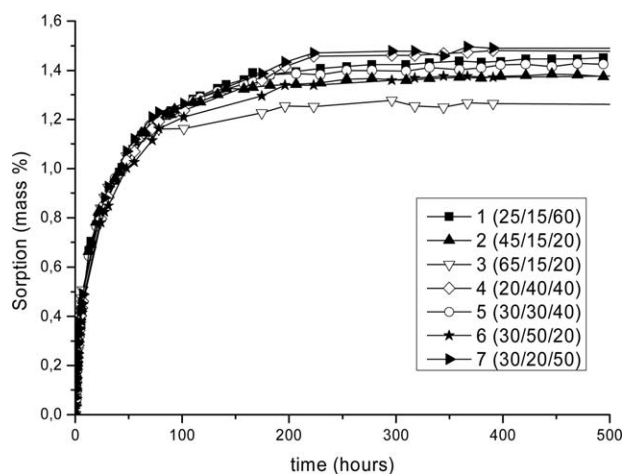


Figure 5. Sorption curves of Chemraz 505 for mixtures Tol/MeOH/Chex: (1) 25/15/60 (■), (2) 45/15/40 (▲), (3) 65/15/20 (▽), (4) 20/40/40 (◻), (5) 30/30/40 (○), (6) 30/50/20 (★), and (7) 30/20/50 (►).

mobility, the small positive deviation to Fick's law may be related to negligible swelling of the polymer. This is not the case of mixture 6 that shows $n = 0.6$, that is positive deviation to Fick's law and consequent swelling, probably related to the presence of bigger amount of methanol in the mixture. Solvent-polymer interaction parameter revealed larger affinity for toluene rather than for cyclohexane and methanol which is more polar and a smaller molecule. Also results obtained for K in mixtures are always higher than those observed for pure cyclohexane and pure methanol, suggesting the increase of molecular interactions of mixtures with the polymer chain segments. In fact, immersion of elastomer in solvent mixtures increased the mass of solvent absorbed as well as sorption rate—while 1% sorption in mixtures is reached before 50 h this value is only closely reached by pure toluene and pure cyclohexane after almost 200 h, showing that the polymer is less resistant to the mixtures than to pure components.

Changes on the microenvironment in the vicinity of the elastomer can be the reason for this behaviour since, in mixtures, diffusion coefficients of species are not independent, so gradients of concentration in one of them, e.g., caused by decrease in concentration generated from the permeation through a barrier like the polymer, may generate concentration gradients of the other solvents in the mixture. From diffusion coefficients data by Grossmann and Winkelmann²¹ it is clear that, for these mixtures, gradients on concentration of toluene generate coupled counter current gradients of cyclohexane. If Toluene is entering the polymer, negative gradients of concentration of this component will be created close to the polymer barrier, generating cyclohexane gradients towards the polymer, hereby compelling this component to also cross to the inside of the polymer and creating a synergetic effect. Even if swelling produced by the sorption of the solvents is not significant for this polymer it could create more available gaps between the backbone structures and enhance sorption. Environment temperature shows to be an important factor since variation between sets of samples can lead to difference in sorption 8 and 14% (increasing at higher temperature). Desorption of liquids from the Chemraz

505 elastomer shows that toluene, cyclohexane, and ternary mixtures are retained in trace amounts within the polymeric network, up to 0.1%, while methanol is totally eliminated.

Diffusion Coefficients

Diffusion coefficients for both pure components and mixtures were determined from the rate of sorption or desorption, for short and long time exposures to the liquids, and are presented on Table III. Examination of the results obtained from application of both eqs. (2) and (3) to sorption data shows that diffusion coefficients in pure liquids follows the order $D_{\text{Tol}} > D_{\text{MeOH}} > D_{\text{CHex}}$. Although toluene and cyclohexane exhibit very close molar volumes (molar volume of toluene = $106.9 \text{ cm}^3 \text{ mol}^{-1}$ and molar volume of cyclohexane = $108.9 \text{ cm}^3 \text{ mol}^{-1}$) they present very different diffusivities.

In the short time (less than 50% sorption) the diffusion coefficients observed for the mixtures follow the order $D_3 > D_7 > D_6 > D_2 > D_5 > D_1 > D_4$ (the subscript number in D stands for the corresponding liquid mixture). Remind, that mixtures 1, 2, 3 contain the same percentage of methanol, i.e., 15%. It appears that a decrease of the diffusion coefficient occurs when the fraction of toluene in the mixture decreases and the fractions of cyclohexane in the mixture increases. If we apply eq. (2) to the desorption data we can observe diffusion coefficients, D_d , that are smaller than the ones obtained from the sorption runs, except for pure methanol and methanol rich mixtures, for which diffusivity of the liquid in desorption can occur almost twice faster than sorption. This might be attributed to the different drying mechanisms included especially by the higher temperature boiling liquids.

If eq. (3) is used to fit sorption data when equilibrium sorption is attained by long time exposure to the solvents, the tendency on the diffusion coefficients D_∞ observed is $D_3 > D_2 > D_6 > D_5 > D_7 > D_1 > D_4$ (Table III). There is a clear general decrease of the observed diffusion coefficient when the Toluene fraction in the mixture diminishes, both when looking at the mixtures

Table II. Sorption Coefficients, Estimated Parameter K and Average Values for n for Chemraz 505 Perfluoroelastomer with Pure Solvents and Tol/MeOH/Chex Mixtures

Liquid	Sorption (mass %)			$K \cdot 10^3 / (\text{g/g} \cdot \text{s}^n)$	
	Room T^a	25 °C	n	Room T^a	25 °C
Toluene	0.90	0.98	0.51	2.25	2.38
Methanol	0.52	0.57	0.51	1.02	1.29
Cyclohexane	1.00	1.11	0.52	1.27	1.34
1		1.45	0.52		1.64
2		1.37	0.50		2.28
3	1.13	1.28	0.51	1.91	2.31
4	1.37	1.48	0.51	1.80	1.62
5		1.43	0.52		1.70
6		1.38	0.61		0.73
7		1.49	0.51		1.74

^aRoom temperature 21 °C.

Table III. Diffusion Coefficients (D) of Sorption and Desorption (D_d) at <55% and at Equilibrium (D_∞) for Pure Liquids and Tol/MeOH/Chex Mixtures

Liquid	$T = 25^\circ\text{C}$			Room T^a	
	$D / (10^{12} \text{ m}^2 \text{ s}^{-1})$	$D_d / (10^{12} \text{ m}^2 \text{ s}^{-1})$	$D_\infty / (10^{12} \text{ m}^2 \text{ s}^{-1})$	$D / (10^{12} \text{ m}^2 \text{ s}^{-1})$	$D_\infty / (10^{12} \text{ m}^2 \text{ s}^{-1})$
Toluene	1.24	0.62	1.51	0.42	0.9
Methanol	0.72	1.08	0.64	0.28	0.27
Cyclohexane	0.40	0.37	0.43	0.15	0.15
1	0.82	0.74	0.95		
2	0.86	0.91	1.10		
3	1.24	1.80	1.44	0.61	1.20
4	0.79	1.56	0.88	0.52	0.67
5	0.84	0.80	0.99		
6	0.91	1.73	1.01		
7	0.98	1.56	0.98		

^aRoom temperature 21°C , standard deviations: $S_D (D, D_d) = 7 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, $S_D (D_\infty) = 5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$.

in general but also when methanol or cyclohexane fraction are kept constant. When toluene fraction is kept constant, a decrease in the methanol fraction leads to a small decrease in the observed diffusion coefficient. Given that toluene seems to play a key role on the diffusivity of the mixtures inside the Chemraz 505 polymer, the dependence of D_∞ on the toluene mass fraction of the mixtures was evaluated, and is presented in Figure 6. Diffusion coefficients for mixtures were plotted against toluene mass fraction. Curve profile was built based on values of D for mixtures 1, 2, and 3 (mixtures with constant methanol mass fraction) and pure toluene. The fact that it is nonlinear may be indicative of the specific interactions between the mixture components and the polymer chain segments. The fitted curve allows closely predicting the diffusion coefficient for other mixture compositions, with less than 4% deviation (mixtures 4, 5, 6, and 7) regarding the obtained experimental values.

$$D = -9.61 \times 10^{-13} c_{\text{Tol}}^2 + 2.01 \times 10^{-12} c_{\text{Tol}} + 4.74 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$$

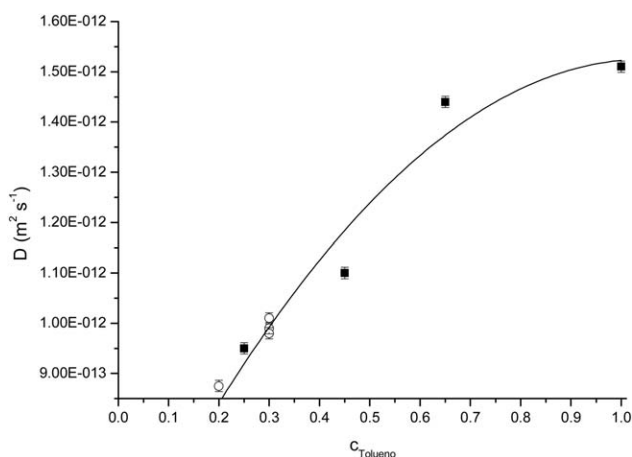


Figure 6. Dependence of diffusion coefficients of mixtures on Chemraz 505 on toluene mass fraction [(■) represents mixtures 1, 2, 3 and pure toluene used to construct the fitting curve and (○) represents mixtures 4–7].

Permeability and Solubility Coefficients

At thermodynamic equilibrium, the permeability coefficient, P , quantifies the volume of penetrant that passes per unit of time through a unit area of polymer having unit thickness, with a unit pressure difference across the system. When a penetrant obeys Fick's law the permeability coefficient P comes described by the solution–diffusion model^{14,22,23} as

$$P = D \cdot S \quad (5)$$

and depends on the solubility coefficient, S [$\text{kg m}^{-3} \text{ Pa}^{-1}$], as well as the diffusion coefficient D [$\text{m}^2 \text{ s}^{-1}$]. Calculations of P for the fluoroelastomer–solvent systems have been done using the values of the solubility S (that comes defined from the saturation plateau of the sorption plot) and the diffusion coefficients at equilibrium sorption D_∞ . The results of P for pure liquids and mixtures (at 25°C) are summarized in Table IV. From the analysis of Table IV, it is perceived that toluene has both permeation and solubility coefficients larger than cyclohexane and methanol whereas, in mixtures, the increase on the toluene fraction leads to increased permeability and decrease in methanol fraction leads to an increase of concentration of diffusing molecules inside the polymer (here represented by the solubility coefficient).

The solution–diffusion model assumes the existence of thermodynamic equilibrium at the interface between the feed mixture and the polymeric membrane and, therefore the thermodynamic interactions between the penetrant and polymer will dictate the level of sorption. A number of various models have been developed to predict the component volume fractions and the interactions of each specific polymer–permeant system, being the Flory–Huggins parameter, χ , one of the leading parameters to represent such kind of interactions.^{24,25} The activity of the penetrant²⁶ inside the polymer according to the Flory–Huggins theory can be given as

$$\ln a_i = \ln \phi_i + \left(1 - \frac{V_m}{V_p}\right) \phi_p + \chi \phi_p^2 \quad (6)$$

where a_i is the activity of the penetrant molecule, ϕ_i the volume fraction of the species, and V_m the molar volume of the solvent.

Table IV. Permeation of Different Solvent and Tol/MeOH/Chex Mixtures through Chemraz 505 Polymers

Liquid	$D_{\infty} / (10^{12} \text{ m}^2 \text{ s}^{-1})$	$S / (10^3 \text{ kg m}^{-3} \text{ Pa})$	$P / (10^{14} \text{ kg m s Pa})$
Toluene	1.51	4.59	6.93
Methanol	0.64	0.62	0.40
Cyclohexane	0.43	0.75	0.68
1	0.95	2.13	2.01
2	1.10	2.28	2.51
3	1.44	2.45	3.52
4	0.88	1.96	1.71
5	0.99	2.00	1.97
6	1.01	1.87	1.88
7	0.98	2.22	2.17

Standard deviations: $S_D(S) = 3 \times 10^{-5} \text{ kg m}^{-3} \text{ Pa}$, $S_D(P) = 4 \times 10^{-16} \text{ kg m s Pa}$.

According to Aminabhavi²⁷ the polymer volume fraction ϕ_p can be calculated from the equilibrium swelling of the membrane (mass %) and, in the ideal solvent approximation ($a_i = 1$) the interaction parameter can be obtained. The χ parameter gives a qualitative estimate of the type of interactions possible between the polymer and the solvent. A value of $\chi > 2$ is considered to be large and associated to small interactions between the chosen pair of polymer–solvent. On the other hand, values of $\chi < 2$ are associated with high interactions between the polymer and the solvent and high permeabilities (for $\chi < 0.5$ solvation may take place due to the polymer and solvent compatibilities). For the liquids under study the values of χ are high (Table V), being methanol the solvent that presents smaller interactions. At constant methanol fraction (or constant cyclohexane fraction), the values for χ increase for increased richness in toluene of the mixtures suggesting weakened thermodynamic interactions with the polymer chain segments. This observation is consistent with the decreasing sorption values for these mixtures (Table II). Furthermore χ decreases for mixtures rich in cyclohexane.

It would be expectable that the liquid less compatible with the polymer has the smallest solubility coefficient. Indeed we can verify in Table IV that for mixtures 6 and 4, containing a higher amount of methanol, solubility coefficient is lower than all the other mixtures. Moreover, when toluene or cyclohexane fraction is kept constant, an increase of the methanol fraction in the mixture causes a decrease in solubility. The unfavorable interactions between the methanol molecules and the polymer may have important energetic contributions to the mixing process, resulting in small concentration inside the polymer. As suggested before, this large difference may be related to the fact that methanol is polar and the other solvents are nonpolar and so, more compatible with the polymer matrix. The solely interaction between solvents in mixtures can affect the transport results, and the analysis of the properties of the mixture, represented by its excess molar volume V^E ,^{28,29} can provide additional information. The excess molar volume comes defined as $V^E = V_m - \sum V_i x_i$, in $\text{cm}^3 \text{ mol}^{-1}$, where V_m and V_i are respectively the molar volumes of the mix-

ture and of pure components and x_i are the molar fraction of the components in the mixture. Binary methanol + cyclohexane³⁰ and toluene + cyclohexane³¹ mixtures show positive V^E at all concentrations, probably due to breakup of alcohol structure as a result of the difficult accommodation of the larger cyclohexane molecule in the first case or to nonspecific repulsive interactions between the species in the second case. However, binary methanol + toluene mixtures show small negative V^E ,^{32,33} suggesting the specific dipole–dipole interactions between the components. The calculated ternary excess volumes for the mixtures under study show positive deviations from ideal behavior, with a maximum V^E for mixture 1 and the smallest value of V^E for mixture 3. This indicates that the ternary mixtures are not ideal and that the presence of the third component (toluene) modifies the nature and degree of molecular interaction between methanol and cyclohexane, namely in overcoming the solubility gap between those components.

In what concerns permeability, that is a measure of how easily a permeant molecule moves through the polymer, and thus involves both kinetic and thermodynamic properties of the polymer–permeant system. Toluene presents high specific interaction with the polymeric matrix and the largest diffusion coefficient; accordingly this liquid should present the largest value for P , as verified. Based on previous analysis for pure liquids, it would be reasonable to find that mixtures with large amount of toluene and cyclohexane would present high values for both solubility and permeation coefficients. On the other side, mixtures with significant amount of methanol, less compatible with the polymer; would present lower permeation across the matrix. Indeed this can be verified in the values present in Table V.

Nevertheless, the experimentally calculated values for total permeation rate in mixtures are smaller (5–28%) than the balanced average of pure species permeation rates, that is, the global synergy between the three components is negative as a result of the selectivity of the membrane toward one component, methanol. This is the result of the fact that the solvents interact with the polymer while they interact together and confirms that estimating

Table V. Density, Flory–Huggings Parameter and Excess Volumes for Pure Solvents and Tol/MeOH/Chex Mixtures through Chemraz 505 Polymers

Liquid	$P / \text{cm}^3 \text{ mol}^{-1}$	χ	$V_m / \text{cm}^3 \text{ mol}^{-1}$	$V^E / \text{cm}^3 \text{ mol}^{-1}$
Toluene	0.86227	2.98	106.90	
Methanol	0.78656	3.39	40.73	
Cyclohexane	0.77390	2.78	108.90	
1	0.79033	2.58	87.10	0.54
2	0.80798	2.64	86.39	0.45
3	0.82785	2.73	85.51	0.21
4	0.78884	2.56	65.29	0.45
5	0.79645	2.60	72.24	0.45
6	0.80158	2.64	58.75	0.18
7	0.79517	2.56	81.47	0.50

Standard deviations: $S_D(\rho) = 5 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, $S_D(\chi) = 2 \times 10^{-2}$, $S_D(V_m, V^E) = 1.5 \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$.

Table VI. Estimated Permeation Fluxes of Tol/MeOH/Chex Mixtures through Chemraz 505 Polymers

Liquid	$J_{\text{Tol}}/10^{-9a}$	$J_{\text{MeOH}}/10^{-9a}$	$J_{\text{Chex}}/10^{-9a}$	$J_{\Sigma}/10^{-9a}$
1	2.52	0.15	0.25	2.92
2	4.61	0.27	0.45	5.33
3	6.75	0.39	0.66	7.81
4	1.51	0.09	0.15	1.75
5	2.53	0.15	0.25	2.93
6	2.07	0.12	0.20	2.39
7	2.85	0.17	0.28	3.29

^a J_T , J_M , J_{Ch} , and J_{Σ} have units $\text{kg m}^{-2} \text{s}^{-1}$.

the permeation flow of a mixture based on the knowledge of the flows of each component taken separately is not straightforward.

Estimated Flows

Among the pure liquids, Toluene has the largest diffusion coefficient in the Chemraz 505 polymer (see Table III). Our experiments showed that the presence of this component has strong impact on the value of the diffusion coefficient of the mixtures. Despite the fact that the mixture 1 contains only 0.25 mass fraction of toluene, its diffusion coefficient approaches to that of pure toluene and is larger than methanol or cyclohexane. So it is particularly interesting to understand the flow of toluene across the Chemraz 505 polymer.

For the particular case of a model cell filled with the liquid and with one sealing barrier, the Chemraz 505 O-ring, a correlation can be made to the pervaporative process explained by the solution–diffusion model,¹⁶ allowing to quantitatively estimate the transport of the solvents across the membrane. The driving force for the transport of the liquids through the membrane is the chemical potential gradient across the membrane. As a result, the flux, J_i , of a component i can be described as:

$$J = -L_i \frac{d\mu_i}{dx} \quad (8)$$

where $d\mu_i/dx$ is the gradient in chemical potential of the component i and L_i is a phenomenological constant linking the chemical potential driving force with flux. The final flux equation for the pervaporative process expressing the driving force in terms of the vapor pressure is

$$j_i = P_i \frac{\Delta p}{l} \quad (7)$$

where J_i is mass flux of the component through the rubber membrane, P_i is the permeability coefficient, Δp is the pressure difference over the membrane and l is permeation path (membrane thickness).³⁴ This driving force can be equally expressed in terms of concentration differences but there is evidence that the use of vapor pressure leads to much more useful results.³⁵

Permeation fluxes estimated from the individual components are presented in Table VI. Flow of toluene across the polymer is the prevailing one for all mixtures with exception of mixture 4 where methanol flow overcomes.

Based in all previous results, kinetic and thermodynamic, it is obvious that there is a important transport of Toluene across the Chemraz 505 polymer, probably due to both its high mobility within the polymer and its high solubility coefficient. Indeed this observation can be useful to explain the results on the experimental preliminary compatibility tests between Chemraz polymer and these toluene, methanol, and cyclohexane mixtures. The Chemraz 505 polymer was used in these tests a sealant (barrier) in a model cell filled with liquid, and exposed for a long time to the mixtures 1, 3, and 4. After 67 days, the liquids inside the model cells showed the first changes either by the formation of vapor bubbles or by demixing of the liquid (see Fig. 2). When the predominant flows in the mixtures 1 and 4 are analyzed it is easily foreseen that the transport of the components across the O-ring forces the composition of the mixture to evolve towards the demixing zone, inherent to this ternary system.⁶ In the case of mixture 3, the ternary V^E values found are higher than in the binary corresponding methanol + cyclohexane and bearing in mind that the flow of toluene is very high, and that this binary mixture presents a solubility gap in wide range of concentrations, the changes in the composition occurring on the mixture when the molar fraction of toluene decreases lead to volume changes that ultimately are the main responsible factor for the appearance of bubbles in the samples.

CONCLUSIONS

Aspects of sorption and desorption kinetics of pure liquids and ternary mixtures of toluene, methanol, and cyclohexane were studied using a gravimetric method. The analysis of the sorption and desorption isotherms and determination kinetic parameters showed the occurrence of a Fickian transport mechanism. Observed sorption by the Chemraz 505 elastomer is higher for mixtures than for individual pure liquids. The diffusion coefficients have been calculated from Fick's equation for short and long time exposure to the liquids. For pure liquids diffusion coefficients followed the order $D_{\text{Tol}} > D_{\text{MeOH}} > D_{\text{Chex}}$ and for mixtures the diffusion coefficients exhibited a systematic dependence on the fraction of Toluene present in the mixture. The gravimetric method used in this study provided not only kinetic but also thermodynamic information from sorption experiments, like the Flory–Huggings parameter, and allowed an evaluation of the potential interactions of the liquids with the polymer. Permeation coefficient increased with the increase of the fraction of toluene in the mixture while solubility coefficient decreased with the increase of the fraction of methanol in the mixture. Methanol showed the smaller solubility coefficient within the polymer together with the highest Flory–Huggings parameter, meaning that the polymer is selective towards this component. A simple approach based on the solution–diffusion model has been used for predicting the transport of the liquids through the Chemraz 505 polymer in a model cell. Observation of vapor bubbles in mixtures 1, 3 and 4 can be explained by the changes in composition motivated by the predominant flows of the components across the polymer and possible occurring volume changes in the mixture. The present study may be useful to field engineers and technologists for a proper selection of the sealings in areas that involve the mixed solvent media.

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