

The Effects of Solvent Polarity and pKa on the Absorption of Solvents into Poly(glutaric acid-glycerol) Films

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ABSTRACT: In this study, solvent absorption into the matrices of poly(glutaric acid-glycerol) films has been evaluated. It was determined that the combined effects of polarity and the size and shape of the solvent molecule, rather than pKa, have the most significant influence on absorption into the films. Polar aprotic solvents (with solvent polarity index values >4) such as 1,4-dioxane (absorbed $163.8\% \pm 0.3\%$ [w/w] of the original weight of the polymer), pyridine ($200.4\% \pm 3.5\%$), and dimethyl sulfoxide ($186.0\% \pm 11.4\%$) were among the highest absorbed solvents into the polymer matrix. Solvents with polarity index values ≤ 4.0 were absorbed poorly ($\leq 5.3\% \pm 1.5\%$). The polymer films only absorbed $\leq 26.5\% \pm 2.1\%$ of their weight of most protic solvents (water and mono-alcohols) but absorbed $72.6\% \pm 6.5\%$ of ethylene glycol, a diol. The only high absorbing polar protic solvent was acetic acid ($131\% \pm 13.1\%$). Except for chloroform, ethyl acetate, and ethanol, all of the solvents examined displayed small increases in absorption (7.8%, on average) when the films were desorbed and used again to absorb solvent. Erosion of the films ranged from $0.0\% \pm 0.0\%$ to $22.0\% \pm 3.2\%$ after 2–10 h absorption cycles. Miscible ($7.7\% \pm 2.3\%$ to $15.1\% \pm 2.2\%$) and immiscible ($12.3\% \pm 6.4\%$ to $80.0\% \pm 1.9\%$) solvents were preferentially absorbed from aqueous solutions. However, up to approximately 5% of those absorption values could be from water absorption. © 2014 Wiley Periodicals, Inc.† J. Appl. Polym. Sci. 2014, 131, 40434.

KEYWORDS: adsorption; biomaterials; biosynthesis of polymers; gels; polyesters

Received 26 September 2013; accepted 21 December 2013

DOI: 10.1002/app.40434

INTRODUCTION

In the early 1970s, researchers at the United States Department of Agriculture (USDA) developed materials based on the grafting of acrylonitrile polymers onto the backbone of starch molecules in a process known as starch-grafting.¹ The hydrolyzed product that resulted from the hydrolysis of this starch-acrylonitrile co-polymer absorbed >400 times its weight in water and later became known as “Super Slurper”.² The study was initially targeted to improve water conservation in soils but it was first used commercially for disposable hygienic products such as feminine sanitary napkins and adult incontinence products. Over the years, starch-grafted super absorbent polymer technologies have been replaced with sodium neutralized, cross-linked acrylic homo-polymers.

Keeping with the theme of agricultural utilization research, we have previously studied the absorption of various solvents into the matrix of poly(glutaric acid-glycerol) films.^{3,4} In our previ-

ous studies, various changes to the physical and chemical environment (i.e., temperature, solvent pH, solvent polarity index [SPI]) affected the absorption of solvents into the film. While several variations of the chemical composition of films were investigated, including amending them with plant cell wall polysaccharides, varying the diacid, and changing the molar ratio of reactants, it was obvious that the polymer films would swell more in polar aprotic solvents like dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) than they would swell in polar protic solvents like methanol and water.

In these previous studies, solvent absorption into the films appeared to be affected by the pKa of the solvent.⁴ When the pKa of a polar aprotic solvent (i.e., t-butyl acetoacetate) was low, solvent absorption into the film was low and similar to that of water. As the pKa of the solvents increased, their absorption into the films also increased. It was observed that if pKa's were similar for two solvents, the solvent with the higher SPI

would be more fully absorbed. Therefore, it was hypothesized that solvent absorption into poly(glutaric acid-glycerol) films could be a function of the pKa and polarity of the solvent. However, our data set was too small to definitively affirm such a relationship. In the present study, 25 solvents with readily accessible literature values for pKa and polarity were investigated to determine if a real relationship exists between the two parameters and absorption into poly(glutaric acid-glycerol) films. It was also of interest to determine if a larger sample size would reveal other trends that could be used to identify the best applications for these films.

One perceived use for solvent-absorbing films made from glycerol is extraction technologies such as water remediation. In previous studies, poly(glutaric acid-glycerol) films were able to absorb a relatively large amount of DMSO. Furthermore, DMSO was preferentially extracted by poly(glutaric acid-glycerol) films when mixed with poorly absorbed solvents like hexane and *t*-butyl acetoacetate.⁴ However, it was unexpectedly observed that the extraction of DMSO from water, another poorly absorbed solvent, was unsuccessful. This observation is likely the result of the solvents' strong intermolecular interactions and miscibility.⁵ However, less polar solvents may be candidates for extraction from water by poly(glutaric acid-glycerol) films. Therefore, one of the goals of this project was to determine if strongly absorbed solvents that are not miscible in water could be extracted from water by the films.

EXPERIMENTAL

Materials

Glutaric acid (99%), reagent grade glycerol (99.9%), reagent grade *t*-butyl acetoacetate (98%), triethylamine (99%), anhydrous THF (99.9%), spectroscopic grade toluene, reagent grade 1-pentanol (99%), anhydrous methyl acetate (99+%), 2-butanone (99%), reagent grade pyridine (99%), HPLC grade methyl *t*-butyl ether (MTBE) (99.9%), anhydrous 1,4-dioxane (99.8%), HPLC grade methyl isobutyl ketone (>99.5%), and spectrophotometric grade DMSO were purchased from Sigma Aldrich (St. Louis, MO). HPLC grade acetone, chloroform, and hexanes (certified ACS) were purchased from Fischer Scientific (Fair Lawn, NJ). HPLC grade 2-propanol and HPLC grade ethyl acetate were purchased from Burdick and Jackson (Muskegon, WI). Anhydrous ethanol (200 proof) was purchased from The Warner-Graham Company (Cockeysville, MD). Acetic acid was purchased from Mallinckrodt (Phillipsburg, NJ). Reagent grade anhydrous ether, reagent grade 1-butanol, and HPLC grade acetonitrile were purchased from J.T. Baker (Phillipsburg, NJ). Aluminum weighing dishes (4" dia. × 5/16" deep) and jars (Qorpak, 2 oz, Straight Side Round Jars with Teflon-Lined Caps) were purchased from Thomas Scientific (Swedesboro, NJ).

Synthesis of Polymer Films

Polymer films were made by first synthesizing polymers from glycerol and glutaric acid using a modified version of a previously described protocol.³ Glutaric acid (1.4 mol) and glycerol (0.7 mol) were reacted for 6 h at 135°C in a 1 L round bottom flask with 460 mL of toluene. A reflux condenser connected to the top of a Dean-Stark apparatus removed water generated by

esterification. Following reaction, the solvent was removed from the crude reaction products by rotary evaporation. These polymers were used to make films that would further react to consume any residual starting material. Therefore, purification at this step was unnecessary.

About 15 g of the reaction mixture consisting of a 2 : 1 molar ratio of glutaric acid : glycerol gel were transferred to individual aluminum weighing dishes and cured in an oven at 135°C for 12 h.

Absorption and Erosion Measurements

Procedure and Calculations. The samples were bored from the aluminum pans into circles that were 1 inch in diameter. The samples were weighed (W_d) and immersed into 15 mL of solvent in capped, 2 oz jars. The samples were removed from the jars after 10 h of incubation at room temperature, blotted with a Kimwipe (Kimberly-Clark, Marietta, GA), and weighed (W_s).

Weight changes due to solvent absorption was determined by the following equation,

$$\% \text{ Weight change} = (W_s - W_d) / W_d \times 100 \quad (1)$$

where W_s and W_d represent the weight of the swelled and dry films, respectively.

Erosion. Erosion is defined as the physical depletion of a material, and is in contrast to degradation which involves chemical bond cleavage. Erosion of the films is calculated from the weight of the film before and after the film has been absorbed and desorbed twice and calculated by the following equation,

$$\% \text{ Erosion} = (W_s - W_{de}) / W_{de} \times 100 \quad (2)$$

where W_{de} represents the weight of the desorbed films.

Polymer Resorption. To evaluate the ability to reuse these materials, the polymer films were allowed to desorb by gravity filtration and solvent evaporation in fume hoods until the polymer films returned to their original weight. If erosion was high, the film would break into pieces and the pieces would be recovered as efficiently as possible.⁴ In such cases, the weight of the desorbed film could be less than the original weight of the film. The desorbed polymer films were then re-submerged into solvent and evaluated for solvent absorption as previously described using eq. (1). The amount of solvent resorbed was expressed relative to the weight of the eroded materials rather than the original weight of the film.

Preferential Organic Solvent Extraction from Aqueous Solutions. To evaluate the ability of these poly(glutaric acid-glycerol) films to extract solvent from water, 2 mL of MTBE, THF, 2-butanone, chloroform, methyl acetate, ethyl acetate, 1,4-dioxane, or acetone were added to 13 mL of tap water. Polymer films bored from the aluminum pans into circles that were 1 inch in diameter were then placed in 2 oz jars and incubated at room temperature for 10 h. Samples were examined for solvent absorption as previously described using eq. (1).

RESULTS AND DISCUSSION

Synthesis

Polymers made by the esterification of glycerol and glutaric acid were prepared by modifying our published synthetic protocol.³ Consistent with the results of previous studies, reacting the diacids in toluene at 135°C gave polymer gels in the form of viscous liquids with the solubility characteristics of similar polymers.^{6,7} These polymers were soluble in polar organic solvents but would not dissolve in water or nonpolar solvents. The resultant films made with a 2 : 1 (glutaric acid : glycerol) molar ratio, lost an average of $7.6\% \pm 0.4\%$ of their initial weight, presumably in the form of water as the by-product of esterification. The final products were clear, flexible, solid materials with a yellow hue. The pre-cured gels and cured films previously made under similar conditions have been extensively characterized by gas chromatography (GC),^{8,9} thermogravimetric analysis (TGA),⁹ Fourier Transform infra-red spectroscopy (FTIR),⁹ and nuclear magnetic resonance spectroscopy (NMR)¹⁰ (¹H and ¹³C).

Absorption Studies

Previously, only seven polar and non-polar solvents were used to investigate absorption into poly(glutaric acid-glycerol) films.⁴ In this study, the number of solvents was increased to 25 constituting a diverse group that would allow the investigation of solvents by pKa,^{11–16} SPI,^{17,18} functional group classes, and molecular size and structure. Previous studies suggested that when aprotic polar solvents have similar pKa's (± 3 units), the solvent with the highest polarity index would absorb the most solvent.⁴ The expanded group of solvents revealed that this correlation remained true when considering a very narrow pKa range (Table I). There was no apparent absorption trend that could uniformly characterize the entire group of solvents. However, there were subsets of data that were informative.

Table II shows that, for the solvents studied, if the solvent polarity was ≤ 4.0 , the absorption was $\leq 5.3\% \pm 1.5\%$. There were no apparent similarities among these solvents to explain this observation as they vary randomly in molecular composition, molecular structure, pKa, dielectric constant, and protic and aprotic character. The only low absorbing solvent with a SPI > 4.0 is methyl isobutyl ketone (SPI = 4.2) which is absorbed into the film at $3.7 (+2.5)\%$ of the film weight. However, there are high and low absorbers at SPI 4.2 and SPI 4.3 which indicates that the absorption into films with polarities above an SPI of 4.0 is intrinsically controlled by phenomena other than polarity.

When the solvents were divided into functional group types, it was clear that two factors influence solvent absorption: polarity and molecular size and shape. Table III shows the film absorption of the alcohols tested in this study. The data reveals that as the polarity of the solvents increases, the absorption into the films also increases. Consequently, an increase in polarity is accompanied by a decrease in chain length of the molecules. Therefore, it appears that the ability of molecules to enter into the matrix of the film could depend on a combination of the solvent polarity and size and shape of the solvent molecules. Methanol (SPI = 6.6) swells the polymer film by $26.5\% \pm 2.1\%$ of its original weight and is the highest absorbing mono-

alcohol. The ability of alcohols to swell the polymer films decreases as the aliphatic chains grow. The films did not swell at all in n-pentanol (SPI = 3.6). Ethylene and propylene glycol were the only diols tested in this study. Ethylene glycol has a higher polarity index (SPI = 6.9) than all of the mono-alcohols studied and absorbs 2.7-fold more solvent than methanol—the highest absorbing mono-alcohol. Since ethylene glycol has two hydroxyl groups, hydrogen bonding could cause it to better “solvate” species within the matrix of the film more readily than a mono-alcohol. However, the poly(glutaric acid-glycerol) films only absorbed $2.3 (\pm 0.5)\%$ of propylene glycol—a diol that is very similar in structure to ethylene glycol. The difference in solvation could be credited to the different conformations of the two diols. Ethylene glycol is linear while propylene glycol is commercially a racemic, non-linear mixture that has an extra methyl group when compared with ethylene glycol. Therefore, propylene glycol could be more sterically restricted from entering the film matrix. The data for propylene glycol is not included in Table II because values for solvent polarity and pKa could not be found. Therefore, this observation cannot be fairly discussed and compared with the absorption data for the other alcohols.

When comparing acetic acid to its methyl and ethyl ester derivatives (methyl and ethyl acetate, respectively), it is clear that solvent polarity and solvent absorption into the poly(glutaric acid-glycerol) film are directly related while molecular size and solvent absorption are inversely related (Table IV). Acetic acid has the highest absorbance or $131.1 (+13.1)\%$ and it is the smallest molecule and highest SPI (SPI = 6.2) within the series. As the carboxylic acid hydrogen is replaced with methyl (SPI = 4.4) and ethyl groups (SPI = 4.3), the absorption decreases with increased chain length and decreased polarity. When compared with solvent absorption in acetic acid, the films absorbed 44.0% and 64.7% less solvent when incubated in methyl acetate and ethyl acetate, respectively.

The trend continued with the ketone series (Table V). Acetone, the simplest ketone, was absorbed into the matrix of the polymer film and swelled it by $77.7 (\pm 2.8)\%$ of its original weight. The ketones became less polar by adding alkyl groups to acetone (SPI = 5.4) to form 2-butanone (SPI = 4.7) and methyl isobutyl ketone (SPI = 4.2). The swelling resulting from solvent absorption was reduced slightly from $77.7 (\pm 2.8)\%$ in acetone to $71.0 (\pm 7.3)\%$ in 2-butanone. Absorption dramatically dropped to $3.7 (\pm 2.5)\%$ for the less polar and larger methyl isobutyl ketone.

The ether series contains both cyclic and aliphatic ethers (Table VI) and these solvents also swell poly(glutaric acid-glycerol) films in amounts directly proportional to their SPI values. The cyclic ethers, THF (SPI = 4.2) and 1,4-dioxane (SPI = 4.8), swelled the polymers to $106.4 (\pm 9.0)$ and $163.8 (\pm 0.3)\%$ of their weight, respectively. It is reasonable to assume that more 1,4-dioxane is absorbed by the films than THF because of the additional oxygen atom available for hydrogen bonding. The cyclic ethers have higher SPI values, are more compact, and their oxygen atoms are more exposed and available for hydrogen bonding than their aliphatic counterparts. Solvent absorption decreased to $2.6 (\pm 0.7)\%$ when the films were incubated

Table I. Absorption of Solvents into Poly(glutaric acid-glycerol) Films Listed by Increasing pKa of the Solvent

Solvent	Structure	pKa	SPI	Absorbance (%)	Reabsorbed (%)	Erosion (%)
Diethyl ether		-3.5 ^a	2.9	2.6 (±0.7)	5.2 (±0.1)	0.0 (±0.0)
MTBE		-2.0 ^a	2.5	0.0 (±0.0)	0.7 (±0.9)	1.8 (±0.7)
1,4-Dioxane		2.1	4.8	163.8 (±0.3)	187.4 (±25.3)	22.0 (±3.2)
Acetic acid		4.75	6.2	131.1 (±13.1)	169.6 (±15.0)	12.4 (±2.7)
Pyridine		5.22 ^a	5.3	200.4 (±3.5)	219.8 (±5.4)	16.5 (±1.3)
t-Butyl acetoacetate		10.0	n/a	1.7 (±0.4)	2.9 (±0.5)	0.0 (±0.0)
Triethylamine		10.67	1.8	5.3 (±1.5)	9.4 (±1.8)	0.0 (±0.0)
Ethylene glycol		14.22	6.9	72.6 (±6.5)	83.5 (±9.5)	5.8 (±3.0)
Chloroform		15.5	4.4	168.9 (±12.9)	147.6 (±5.2)	0.0 (±0.0)
Water		15.8	9.0	4.7 (±1.2)	5.6 (±1.3)	7.6 (±1.3)
Methanol		15.5	6.6	26.5 (±2.1)	26.8 (±1.9)	9.1 (±1.2)
Ethanol		15.9	5.2	18.6 (±0.4)	15.7 (±0.5)	2.8 (±0.3)
Isopropanol		16.5	4.3	10.0 (±2.0)	14.3 (±2.2)	0.0 (±0.0)
n-Butanol		16.1	4.0	2.4 (±1.2)	4.1 (±1.2)	0.0 (±0.0)
n-pentanol		16.8	3.6	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
Methyl isobutyl ketone		19.6	4.2	3.7 (±2.5)	4.8 (±1.8)	1.8 (±0.6)
Acetone		19.7	5.4	77.7 (±2.8)	84.5 (±1.5)	16.7 (±0.5)
2-Butanone		20	4.7	71.0 (±7.3)	80.8 (±3.4)	10.8 (±1.8)
Ethyl acetate		21	4.3	46.3 (±5.3)	35.1 (±6.2)	12.0 (±1.1)
Methyl acetate		25	4.4	73.4 (±3.5)	84.2 (±2.5)	11.6 (±0.5)
Acetonitrile		28.9	6.2	57.8 (±9.3)	66.1 (±4.2)	11.8 (±1.5)
DMSO		35	6.5	186.0 (±11.4)	203.0 (±8.9)	2.1 (±0.8)
THF		38	4.2	106.4 (±9.0)	113.3 (±12.7)	19.3 (±0.9)
Toluene		38	2.4	2.6 (±0.8)	4.3 (±1.0)	0.0 (±0.0)
Hexane		60	0.0	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)

^apKa of the conjugate acid.

in diethyl ether (SPI = 4.3) and to 0.0 (±0.0)% when incubated in MTBE (SPI = 2.5).

Table VII lists the solvents that can be characterized, relatively, as well absorbed. Solvents that doubled the weight of their host films were arbitrarily given the high absorber designation. None of the solvents from the alcohol or ketone groups were among the high absorbers and only 6 of the 25 solvents studied were high absorbers. From the molecules discussed so far, acetic acid and the cyclic esters (THF and 1,4-dioxane), were designated as

three of the six high absorbers. The other three high absorbing solvents were chloroform, pyridine, and DMSO which swelled the films by 168.9 (+12.9)%, 200.4 (+3.5)%, and 203.0 (+8.9)%, respectively. While these molecules are either small or heterocyclic, there was no apparent connection among the solvents to explain their affinity to the matrix of the film.

Resorption and Erosion Studies

Resorption studies were performed on the polymer films that had been recovered after solvent desorption. Generally, complete

Table II. Absorption of Solvents (SPI \leq 4.0) into Poly(glutaric acid-glycerol) Films














Solvent	Structure	pKa	SPI	Absorption (%)	Reabsorbed (%)	Erosion (%)
t-Butyl acetoacetate		10.0	n/a	1.7 (\pm 0.4)	2.85 (+0.5)	0.0 (+0.0)
Hexane		60	0.0	0.0 (\pm 0.0)	0.0 (\pm 0.0)	0.0 (\pm 0.0)
Triethylamine		10.67	1.8	5.3 (\pm 1.5)	9.4 (\pm 1.8)	0.0 (\pm 0.0)
Toluene		38	2.4	2.6 (\pm 0.8)	4.3 (\pm 1.0)	0.0 (\pm 0.0)
MTBE		-2.0	2.5	0.0 (\pm 0.0)	0.7 (\pm 0.9)	1.8 (\pm 0.7)
n-Pentanol		16.8	3.6	0.0 (\pm 0.0)	0.0 (\pm 0.0)	0.0 (\pm 0.0)
n-Butanol		16.1	4.0	2.4 (\pm 1.2)	4.1 (+1.2)	0.0 (\pm 0.0)

Table III. Absorption of Alcohols into Poly(glutaric acid-glycerol) Films

Solvent	Structure	pKa	SPI	Absorption (%)	Reabsorbed (%)	Erosion (%)
n-Pentanol		16.8	3.6	0.0 (\pm 0.0)	0.0 (\pm 0.0)	0.0 (\pm 0.0)
n-Butanol		16.1	4.0	2.4 (\pm 1.2)	4.1 (\pm 1.2)	0.0 (\pm 0.0)
Isopropanol		16.5	4.3	10.0 (\pm 2.0)	14.3 (\pm 2.2)	0.0 (\pm 0.0)
Ethanol		15.9	5.2	18.6 (\pm 0.4)	15.7 (\pm 0.5)	2.8 (\pm 0.3)
Methanol		15.5	6.6	26.5 (\pm 2.1)	26.8 (\pm 1.9)	9.1 (\pm 1.2)
Ethylene glycol		14.22	6.9	72.6 (\pm 6.5)	83.5 (\pm 9.5)	5.8 (\pm 3.0)

solvent desorption was achieved within 2 h of removing the film from the solvent. It has been previously observed that, in some cases, eroded polymer films resorb more than three-fold the amount of solvent than the original polymer film.⁴ In this study, the solvents resorbed, on average, 7.8% more solvent than they originally absorbed. The only exceptions were ethanol, ethyl acetate, and chloroform which absorbed 2.9%, 11.2%, and 21.3% less solvent during the resorption cycle. Interestingly, the change in absorption did not change the previously established absorption trends. In contrast to observations for prior absorption studies,⁴ none of the resorption values were dramatically greater than that of the original film.

Erosion was low for all of the low absorbing solvents with SPI \leq 4.0, with all of them except one (MTBE) showing no erosion at all. Erosion was highest among the high absorbing solvents but the % erosion for those varied, on average, from 0.0% to 22%. This information is valuable because, dependent upon the desired applications, films that absorb and maintain their chemical, phys-

ical, and mechanical integrity are just as important as films that absorb for long periods of times followed by erosion. The former properties are attractive for filtration applications while the latter would make good candidates for controlled-release materials.¹⁹⁻²¹

Preferential Organic Solvent Extraction from Aqueous Solutions

Previous studies involving absorption into poly(glutaric acid-glycerol) films showed that DMSO could be preferentially extracted from poorly absorbed solvents such as t-butyl acetoacetate and hexane.⁴ However, only 1.4 (\pm 0.7)% DMSO was extracted from water because, even though DMSO is a well absorbed solvent (Table VII), the intermolecular interactions of the two liquids with each other are likely stronger than the interactions available to them within the polymer matrix.

In this study, additional extractions from water were investigated (Table VIII). Solvents that were either miscible (THF, 1,4-dioxane, and acetone) or immiscible (MTBE, ethyl acetate,

Table IV. Absorption of Acetic Acid its Methyl and Ethyl Derivatives into Poly(glutaric acid-glycerol) Films




Solvent	Structure	pKa	SPI	Absorption (%)	Reabsorbed (%)	Erosion (%)
Ethyl acetate		21	4.3	46.3 (\pm 5.3)	35.1 (\pm 6.2)	12.0 (\pm 1.1)
Methyl acetate		25	4.4	73.4 (\pm 3.5)	84.2 (\pm 2.5)	11.6 (\pm 0.5)
Acetic acid		4.75	6.2	131.1 (\pm 13.1)	169.6 (\pm 15.0)	12.4 (\pm 2.7)

Table V. Absorption of Acetone and Alkyl Derivatives into Poly(glutaric acid-glycerol) Films








Solvent	Structure	pKa	SPI	Absorption (%)	Reabsorbed (%)	Erosion (%)
Methyl isobutyl ketone		19.6	4.2	3.7 (± 2.5)	4.8 (± 1.8)	1.8 (± 0.6)
2-Butanone		20	4.7	71.0 (± 7.3)	80.8 (± 3.4)	10.8 (± 1.8)
Acetone		19.7	5.4	77.7 (± 2.8)	84.5 (± 1.5)	16.7 (± 0.5)

Table VI. Absorption of Aliphatic and Cyclic Ethers into Poly(glutaric acid-glycerol) Films

Solvent	Structure	pKa	SPI	Absorption (%)	Reabsorbed (%)	Erosion (%)
MTBE		-2.0	2.5	0.0 (± 0.0)	0.7 (± 0.9)	1.8 (± 0.7)
Ether		-3.5	2.9	2.6 (± 0.7)	5.2 (± 0.1)	0.0 (± 0.0)
THF		38	4.2	106.4 (± 9.0)	113.3 (± 12.7)	19.3 (± 0.9)
1,4-Dioxane		2.1	4.8	163.8 (± 0.3)	187.4 (± 25.3)	22.0 (± 3.2)

chloroform, methyl acetate, and 2-butanone) with water were selected for this study. When comparing the water-miscible solvent systems, the film was able to extract 15.1 (± 2.2)% of the THF from water, 10.8 (± 2.4)% from acetone, and 8.3 (± 2.4)% from 1,4-dioxane. These values are considerably lower than the amounts the films swelled in the neat solvents. This suggests that, as observed with the water-DMSO system, intermolecular interactions in the water-solvent systems are preferred over the interactions they would form within the matrix of the film. This theory is further supported when comparing the extraction of the two cyclic esters. It is shown (Table VIII) that THF was more readily extracted from water than was 1,4-dioxane. 1,4-Dioxane should hydrogen bond stronger and become more solvated in water because it has two oxygen atoms available for hydrogen bonding compared with the lone oxygen atom on the THF; thereby, retarding entry of the 1,4-dioxane into the film matrix to a greater extent than THF absorption.

For the immiscible solvents, the absorption trends are inversely proportional to their ability to dissolve in water. Solubility relates to the intermolecular interactions between two solvents and it is, therefore, reasonable to assume that the more a solvent dissolves in water, the stronger the intermolecular interactions are that exist between water and solvent. For the polar immiscible solvents, the solvation trends in water, as listed by the Chemical Abstracts Service in the open scientific literature at 20°C, were 2-butanone (29.0 g/100 mL H₂O) > methyl acetate (25 g/100 mL H₂O) > ethyl acetate (8.0 g/100 mL H₂O) > chloroform (0.8 g/100 mL H₂O). The average percent absorption into the films resulting from extractions from water shows the exact opposite trend (Table VIII). The data showed that the absorption of chloroform (80.0%) > ethyl acetate (55.6%) > methyl acetate (20.5%) > 2-butanone (12.3%). This further supports the theory that strong intermolecular interactions between water and another solvent retards absorbance into the film matrix. Chloroform, 1,4-dioxane, and THF were the

Table VII. Solvents Best Absorbed by Poly(glutaric acid-glycerol) Films















Solvent	Structure	pKa	SPI	Absorption (%)	Reabsorbed (%)	Erosion (%)
1,4-Dioxane		2.1	4.8	163.8 (± 0.3)	187.4 (± 25.3)	22.0 (± 3.2)
Acetic acid		4.75	6.2	131.1 (± 13.1)	169.6 (± 15.0)	12.4 (± 2.7)
Pyridine		5.22	5.3	200.4 (± 3.5)	219.8 (± 5.4)	16.5 (± 1.3)
Chloroform		15.5	4.4	168.9 (± 12.9)	147.6 (± 5.2)	0.0 (± 0.0)
DMSO		35	6.5	186.0 (± 11.4)	203.0 (± 8.9)	2.1 (± 0.8)
THF		38	4.2	106.4 (± 9.0)	113.3 (± 12.7)	19.3 (± 0.9)

Table VIII. The Use of Poly(glutaric acid-glycerol) Films to Extract Solvents From Water

Solvent	Structure	pKa	SPI	Absorption (%)
MTBE		-2.0	2.5	7.7 (+2.3)
THF		38	4.2	15.1 (± 2.2)
Ethyl acetate		21	4.3	55.6 (± 3.9)
Chloroform		15.5	4.4	80.0 (± 1.9)
Methyl acetate		25	4.4	20.5 (± 2.9)
2-Butanone		20	4.7	12.3 (± 6.4)
1,4-Dioxane		2.1	4.8	8.3 (± 2.4)
Acetone		19.7	5.4	10.8 (± 2.4)

only well-absorbed solvents chosen for this study. However, chloroform was the only one of the three to be significantly extracted from the water by the poly(glutaric acid-glycerol) films as the chloroform–water incubated film swelled by $80.0\% \pm 1.9\%$. Chloroform is not miscible with water and was therefore more easily extracted.

MTBE was the only non-polar, poorly absorbed solvent (Table II) that we attempted to extract from water. As expected, extraction of MTBE was low at 7.7 (+2.3)%. In fact, it is likely that water was also absorbed into the film because, comparing the absorption data of MTBE and water (Table I), it is unlikely that MTBE alone can swell the film to that extent. It is reasonable to assume that swelling of the other films that were incubated in water–immiscible solvent systems were not primarily due to water absorption because the absorption trends for the solvents in the mixtures were the same as they were when the films were incubated in the pure solvents. Also, previous studies have shown that the absorption of water into poly(glutaric acid-glycerol) films maximizes at approximately 5% after 10 h of incubation.⁴

CONCLUSIONS

This research shows that there is a correlation among polarity, molecular size and shape, and solvent absorption into poly(glutaric acid-glycerol) films. These films were shown to absorb, on average, 0.0%–219.8% solvent with <22% erosion after 2–10 h incubations. It also shows that the original hypothesis that suggested a correlation existed among pKa, polarity, and absorption, observed with the smaller data set, could not be used to reliably predict solvent absorption into poly(glutaric acid-glycerol) films. While the underlying reason for solvent absorption is still unclear, it was shown that among functional group classes that polarity and molecular size and shape can be used to accurately predict which solvents should be more readily absorbed into poly(glutaric acid-glycerol) films.

Aprotic polar solvents were successfully extracted from aqueous mixtures. Future research in this area should focus on develop-

ing analytical methods capable of quantifying the amount of solvent extracted from water and determining the structural and chemical composition of the film matrix. Because hydrogen bonding seems to play a role in solvent absorption, solvent interaction tools such as Hansen solubility parameters that include hydrogen bonding as a metric within the model could be worthwhile to evaluate on these systems.

ACKNOWLEDGMENTS

Mr. Kerby Jones and Dr. Helen Ngo are acknowledged for providing me with an array of useful solvents.

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