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Swelling Performance Studies of Acrylamide/Potassium 3-Sulfopropyl Methacrylate/Sodium Alginate/Bentonite Biohybrid Sorbent Hydrogels in Binary Mixtures of Water-Solvent

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Abstract

In this study, it was to investigate the swelling performance of novel biohybrid composite hydrogel sorbents containing acrylamide/potassium 3-sulfopropyl methacrylate/sodium alginate/bentonite in water and binary mixtures of water-solvent. Novel hydrogels were synthesized with free radical solution polymerization by using ammonium persulfate/*N,N,N',N'*-tetramethylethylenediamine as redox initiating pair in presence of poly(ethylene glycol) diacrylate as crosslinker. Swelling experiments were performed in water and binary mixtures of water-solvent (acetone, methanol and tetrahydrofuran) at 25˚C, gravimetrically. Some swelling and diffusion properties of the hydrogels were calculated and they were discussed for the biohybrid/hybrid hydrogel systems prepared under various formulations. It has been seen the lower equilibrium percentage swelling ratio values (62% - 124%) in all solvent compositions in comparison with the equilibrium percentage swelling ratio values in water (718% - 2055%). Consequently, the hydrogel systems developed in this study could serve as a potential device for water and water-solvent binary mixtures.

Keywords

Acrylamide/Potassium 3-Sulfopropyl Methacrylate, Biohybrid Hydrogel, Swelling, Sodium Alginate, Bentonite, Water-Solvent Binary Mixtures

1. Introduction

Recently, novel functional materials such as hybrid/biohybrid composite polymers are new materials which have produced properties wanted through the development of specialized areas. Polymer/clay or polymer/zeolite hybrid composite polymeric systems have received great attention because of their relatively low production cost and high adsorption capacity for water, dyes and metals [1]-[8]. Hydrophilic highly swollen crosslinked copolymers called "hydrogels" are synthesized by free radical crosslinking copolymerization with some multifunctional crosslinkers with some co-monomers including hydrophilic groups for increasing of their swelling capacity. A hydrogel can be defined as a polymeric material that exhibits the ability to swell in water and retains a significant fraction of water within its structure without dissolving. Hydrogels are three-dimensional networks of hydrophilic polymer chains with properties in between liquids and solids. Swelling or water sorption property of hydrogels accounts for a great number of biomedical and technological applications. One of the most interesting features is their capability to swell as well as to shrink depending on their surroundings [8] [9]. Hydrogels that are responsive to specific molecules, such as some physiological fluids or biochemical species can be used as biosensors as well as in drug delivery systems and in aqueous solvent mixtures [10]-[20]. Hydrogels are usually sensitive to the solvent medium composition. When a non-water-miscible solvent is added to the water-swollen hydrogel, it often shrinks or collapses. Depending on the gel chemical structure, the solvent nature and water-solvent composition, the gel shrinkage may be gradual (continuous) or abrupt (discontinuous) [13]-[20].

For water treatments, the advantages of hybrid hydrogels have been used as adsorbent. Especially, incorporation of the natural materials into hybrid hydrogels lowers the cost of water purification or treatment, which is the focus of water treatment industry. Polymer/clay hybrid composite hydrogels have received great attention because of their relatively low production cost and high adsorption capacity for some dyes and metal ions [21]-[26]. In many previous studies, several kinds of many absorbent composites based on some clay such as montmorillonite, kaolin, attapulgite, and mica sericite were prepared, and these superabsorbent composites showed high water absorbency and water retention, good salt-resistance, and low production costs in comparison with pure organic superabsorbent polymers under the same preparation condition [21]-[26]. Bentonite (BENT) is a type of clay mainly composed of montmorillonite that is a 2:1 type aluminosilicate. It has a crystalline structure with an octahedral layer of aluminum hydroxide between two tetrahedral layers of silica [21] [26].

Sodium alginate, (SAL) is a natural, renewable, a non-toxic and naturally biodegradable polymer which has gained great attention in many scientific and industrial applications [21] [27] [28]. SAL produced from rich resource of brown algae is an ionic polymer of polysaccharides, and its molecular chains contain a large number of carboxyl and hydroxyl groups [21] [27] [28]. In near neutral aqueous solution, SAL is negatively charged from the ionization of its carboxyl groups [21] [27] [28].

The present paper deals with a preliminary report about swelling properties of a series of a novel hybrid/biohybrid composite hydrogel sorbent system containing polysaccharide/clay polyelectrolyte based on acrylamide (AAm)/potassium 3-sulfopropyl methacrylate (KSM) and SAL, and a clay such as BENT. In our previous paper, it has been reported swelling and dye sorption characterization of AAm/KSM/SAL/BENT hybrid/biohybrid hydrogels [21]. Here, AAm is a highly hydrophilic monomer, KSM is anionic monomer and SAL is a natural polymer. In this respect, a series of copolymeric hydrogels were synthesized by changing the content of KSM, SAL and BENT. Then, some swelling, and some diffusional properties of AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT and AAm/KSM/BENT/SAL hybrid composite hydrogels were studied in water and in binary mixtures of water-solvent by dynamic swelling studies for swelling characterization. Then swelling performance of the hydrogels was investigated in water and in binary mixtures of water-solvent (acetone, methanol and tetrahydrofuran) as a function of chemical composition of the hydrogels.

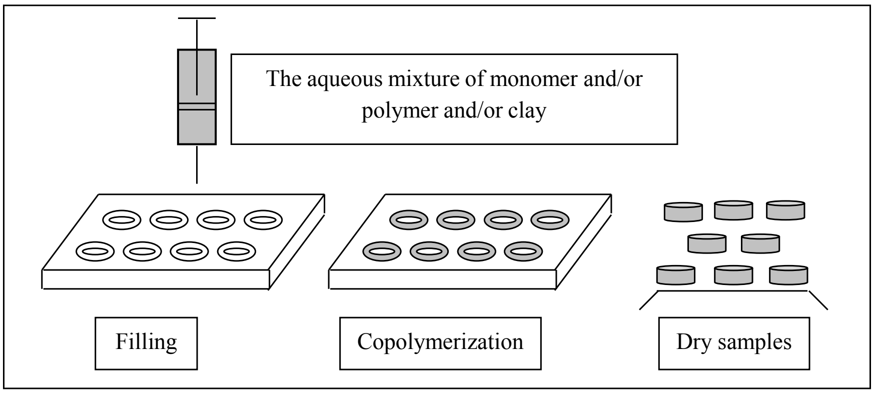
2. Materials and Methods

2.1. Preparation

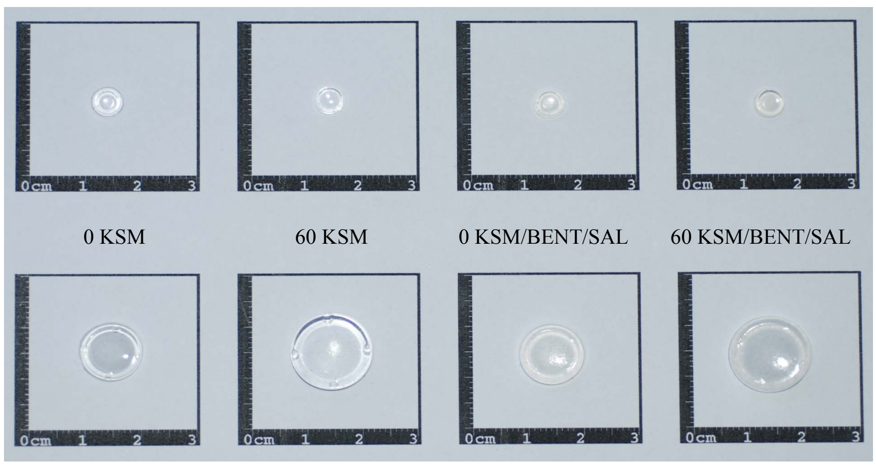
Acrylamide (AAm), the initiator, ammonium persulfate (APS), supplied by *Merck*, (Darmstad, Germany), the activator *N,N,N',N'*-tetramethylethylenediamine (TEMED) were supplied by *Merck*, (Schuchardt, Germany). Anionic co-monomer such as potassium 3-sulfopropyl methacrylate (KSM) (Aldrich, Steinheim, Germany) and a multifunctional crosslinker such as poly(ethylene glycol) diacrylate (PEGDA, M_n = 700) as a crosslinker were supplied from Aldrich, Steinheim, Germany, and sodium alginate (SAL) was purchased from Sigma, Steinheim, Germany. Bentonite (BENT) was purchased from Aldrich, Steinheim, Germany. All chemicals were used as received [21]. The solvents that used in swelling studies, including acetone (ACE), methanol (MET) and tetrahydrofuran (THF), were supplied by Riedel de Haën, Germany. Chemically crosslinked AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid hydrogels, and AAm/KSM/SAL/BENT biohybrid hydrogels were prepared by free radical crosslinking copolymerization of AAm monomer with addition of an anionic comonomer such as KSM and a multifunctional crosslinker such as PEGDA. The modes of purification and specifications of the sources of water, the monomers such as AAm and KSM, crosslinker such as PEGDA, initiator such as APS and activator such as TEMED were given in our related study [21]. In our previous study, the water sorption and dye uptake properties of highly swollen AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid hydrogels, and AAm/KSM/SAL/BENT biohybrid hydrogels have been reported [21]. Briefly the procedures were described below.

To prepare AAm hydrogel systems, AAm weighing 1.0 g (14.07 mmol) was dissolved in 1.0 mL water. Then, 20 mg (0.081 mmol) of KSM were added to aqueous other AAm solution (for AAm/KSM hydrogels containing 20 mg KSM) at room temperature, (25˚C). Then, 40 mg (0.162 mmol), 60 mg (0.243 mmol), 80 mg (0.324 mmol) of KSM were added to other aqueous AAm solutions, respectively for containing different amount of KSM in AAm/KSM hydrogel systems. After these additions, for the synthesis, 0.25 mL (0.004 mmol) of 1.0% concentration of PEGDA and 0.2 mL (0.044 mmol) aqueous solutions of APS (5.0 g/0.022 mmol of APS in 100 mL water) and 0.25 mL (0.017 mmol) 1.0% concentration of TEMED were added these aqueous solutions. In preparation, the solutions were placed in special cylindrical plastic molds (having 7.0 mm of diameter and 3.0 mm of height) (**Figure 1(a)**), then, they were waited for an hour for gelation. After gelation, the samples were washed with distilled water by several times. Then, they were dried in air and vacuum, and stored for swelling studies [21] [24] [26].

For the synthesis of AAm/KSM/SAL semi IPNs, they were prepared by using the same preparation method. But, 0.5 mL of water and 0.5 mL of 2.0% aqueous SAL solution was used instead of 1.0 mL of distilled water in the related preparation



(a)



(b)

Figure 1. (a) Schematic representation of the preparation of the hydrogel systems; (b) The photographs of AAm/KSM hydrogels and AAm/KSM/BENT/SAL hybrid hydrogels (as dry state or swollen state in water) [21].

method. To prepare highly swollen AAm/KSM/SAL (containing different amounts of SAL) semi IPNs, the same method was used as mentioned above with addition of 0.25 mL, 0.75 mL, and 1.0 mL of aqueous solution of 2.0% of SAL to 0.75 mL, 0.25 mL and 0.0 mL water containing of 1.0 g AAm and 60 mg KSM [21].

AAm/KSM/BENT hybrid composite hydrogel systems were prepared by using the similar procedures. 0.5 mL of distilled water and 0.5 mL of 2.0% of BENT/water suspension system was used instead of 1.0 mL of distilled water in the related preparation method. For AAm/KSM/BENT (containing different contents of BENT) hydrogel systems, the same method was used as mentioned above with addition of 0.25 mL, 0.75 mL, and 1.0 mL of 2.0% of BENT/water suspension system to 0.75 mL, 0.25 mL and 0.0 mL water containing of 1.0 g of AAm and 60 mg KSM [21].

AAm/KSM/BENT/SAL hybrid composite hydrogel systems were prepared by using the same preparation method, except that 0.5 mL 2.0% of aqueous SAL solutions and 0.5 mL of 2.0% of BENT/water suspension system was used instead of 1.0 mL of distilled water in the related preparation method [21].

2.2. Swelling Experimental Studies

For dynamic swelling studies, the dried hydrogel systems were accurately weighted and transferred into water solution at 25˚C ± 0.1˚C in a water bath. Water uptake with respect to time was obtained by periodically removing the samples from water followed by quickly blot drying and reweighing. The dried hydrogels were immersed in water, pure solvents, such as ACE, MET and THF, and water-solvent (ACE, MET and THF) binary mixtures at various compositions. The gravimetric method was employed to study the swelling characterization. Swollen gels were removed from water, pure solvents or binary mixtures of water-60% of solvent (ACE, MET and THF) at predetermined times, blotted dry and weighed again. Water, pure solvents and water-solvent binary mixtures were kept at 25˚C ± 0.1˚C to allow the hydrogels to reach equilibrium for solvent composition effect on swelling properties of the hydrogels.

In the next swelling tests, for the investigation of the effect of composition of solvent on swelling, highly swollen AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid hydrogels, and AAm/KSM/SAL/BENT biohybrid hydrogels containing 60 mg KSM have been swollen in binary mixtures of various compositions such as water-20%; 40%; 60% and 80% of solvent (ACE, MET and THF). From these measurements, some swelling and diffusion parameters have been determined.

3. Results and Discussion

3.1. Swelling Characterization

The water, some solvents such as ACE, MET and THF, or some liquids such as water-solvent binary mixtures intake of initially dry hydrogels was followed for novel AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid hydrogels, and AAm/KSM/SAL/BENT biohybrid hydrogels. The hydrogels were waited in water, in solvents and in binary mixtures of various compositions of water-solvent (ACE, MET and THF). Here it was seen that there is no swelling in 100% composition of the solvents such as ACE, MET and THF.

There have been presented the photographs of AAm/KSM hydrogels and AAm/KSM/BENT/SAL hybrid composite hydrogels in Figure 1(b) as dry state or swollen state. The capacity of swelling of the hydrogels can be seen from Figure 1(b) [21].

The water or binary mixtures of various compositions of water-solvent (ACE, MET and THF) intake of initially the hydrogels was followed for a period of time, gravimetrically. Percentage swelling ratio (S%) of the hydrogels in distilled water or binary water-solvent mixtures was calculated from the following relation [21].

$$S\% = \frac{m_t - m_0}{m_0} \times 100 \quad (1)$$

where m_t and m_0 are the mass of the swollen gel at time t and 0, respectively. The liquid intake of initially dry hydrogels was followed for novel AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid hydrogels, and AAm/KSM/SAL/BENT biohybrid hydrogels in water or binary mixtures of water-solvent (ACE, MET and THF. For swelling characterization, swelling isotherms of AAm/KSM hydrogels in water-60% of MET have shown in Figure 2 as representative. As shown in Figure 2, AAm/KSM hydrogels have the lower values of S% in water-60% of MET.

Figure 2 shows that swelling or sorption of liquid increases with time up to certain level, and then levels off. This value of percentage swelling ratio (S%) may be called as the "equilibrium percentage swelling ratio" (S_{eq}%). The values

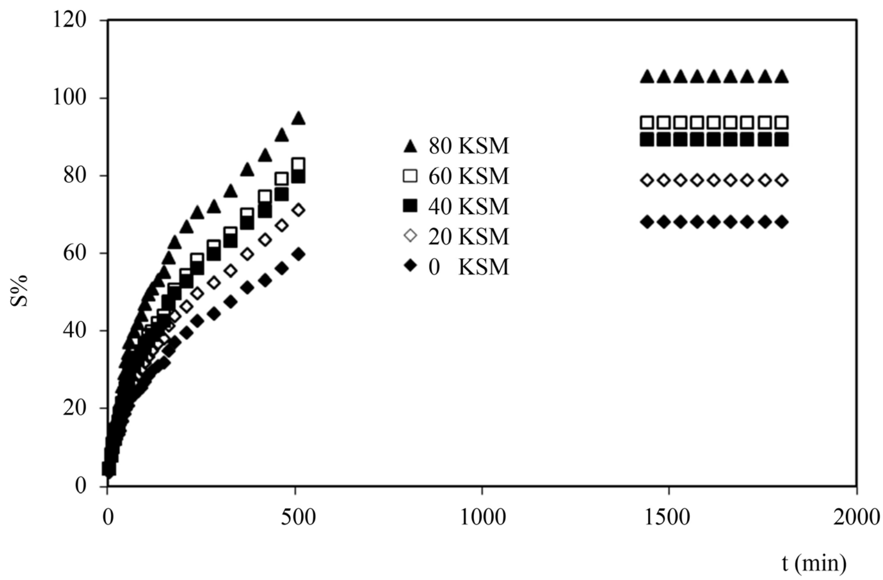


Figure 2. Swelling isotherms of AAm/KSM hydrogels in binary mixtures of water-60% of MET.

of S_{eq}% of the hydrogel systems are given in **Table 1**. **Table 1** shows that S_{eq}% of AAm hydrogels is 808, but S_{eq}% of AAm/KSM hydrogels are 1074% - 2040% with the incorporation of KSM groups into chemically crosslinked AAm copolymers in water. Again, **Table 1** shows that S_{eq}% of AAm hydrogels is 76%, but S_{eq}% of AAm/KSM hydrogels are 84% - 124% with the incorporation of KSM groups into chemically crosslinked AAm copolymers, if AAm/KSM hydrogels have been swollen in binary mixture of water-60% of ACE. The other S_{eq}% values of the hydrogels have been presented in **Table 1** for binary mixture of water-60% of MET and binary mixture of water-60% of THF, too.

In **Table 1**, the values of S_{eq}% of the hydrogels increased with KSM content in the hydrogel systems. Hydrophilicity of KSM molecules becomes greater than that of AAm, and, therefore, the swelling of AAm/KSM is greater than the swelling of AAm hydrogels. AAm/KSM hydrogels contain strong electrostatic interactions within the structure due to many strongly charged groups of KSM units [21]. The swelling increase is probably due to an increase in the anionic properties. Here, the main effect is the hydrophilic characteristics of KSM. It is well

Table 1. The values of S_{eq}% in water or binary mixture of water-solvent (ACE, MET and THF).

KSM/mg	0	20	40	60	80
	Equilibrium percentage swelling ratio (S_{eq}%)				
	Water				
AAm/KSM	808	1074	1357	1735	2040
AAm/KSM/BENT	802	1104	1315	1690	2015
AAm/KSM/SAL	759	1030	1322	1667	1916
AAm/KSM/BENT/SAL	718	1017	1179	1479	1905
	Water-60% of ACE				
AAm/KSM	76	84	92	99	111
AAm/KSM/BENT	82	90	97	101	105
AAm/KSM/SAL	82	99	109	112	124
AAm/KSM/BENT/SAL	80	91	107	112	117
	Water-60% of MET				
AAm/KSM	68	79	89	94	106
AAm/KSM/BENT	67	78	89	92	97
AAm/KSM/SAL	66	69	71	81	85
AAm/KSM/BENT/SAL	62	68	72	75	79
	Water-60% of THF				
AAm/KSM	73	85	94	98	108
AAm/KSM/BENT	81	85	95	98	107
AAm/KSM/SAL	75	89	94	96	100
AAm/KSM/BENT/SAL	76	85	95	98	101

known that the swelling of a hydrogel is induced by the electrostatic repulsion of the ionic charges of its network. The ionic charge content is important. The salt group is almost completely ionized, and a large number of hydrophilic group occur [21]. When the water solvent mixtures were used, the swelling decreases significantly as shown in **Table 1**. The values of S_{eq}% of the AAm/KSM hydrogels are 76% - 111% for water-60% of ACE, 68% - 106% for water-60% of MET, and 73% - 108% for water-60% of THF. Here, the reason of this decreasing of the values of S_{eq}% of the hydrogels is the hydrophobic character of the solvents. The hydrophobic property increases with the increasing of alkyl group of the organic molecular forming in gel structure. For this reason, the more hydrophobic groups in the solvents gave the less the swelling of the hydrogels in binary mixtures of water-solvent (in ACE, in MET and in THF). With the increasing of hydrophobic character of the swelling media, it can be seen that the gel shrinkage. Here for the gel shrinkage, the important reason, the hydrophobic character of the alkyl groups in the molecular structure.

The values of S_{eq}% of the AAm/KSM/BENT hybrid composite hydrogels containing 1.0% of BENT are 1104 - 2015 with the incorporation of BENT groups into AAm/KSM hydrogels, while the value of S_{eq}% of AAm/BENT hybrid composite hydrogels is 802. **Table 1** shows that the values of S_{eq}% of the AAm/KSM/BENT hybrid composite hydrogels are 82% - 105% for water-60% of ACE, 67% - 97% for water-60% of MET, and 81% - 107% for water-60% of THF. On the other hand, the values of S_{eq}% of AAm/KSM/SAL semi-IPNs containing 1.0% of SAL are 1030 - 1916 with the incorporation of SAL into AAm/KSM hydrogels, while S_{eq}% of AAm/SAL semi IPNs is 759. **Table 1** shows that the values of S_{eq}% of the AAm/KSM/SAL semi-IPN hydrogels are 82% - 124% for water-60% of ACE, 66% - 85% for water-60% of MET, and 75% - 100% for water-60% of THF.

The values of S_{eq}% of the AAm/KSM/BENT/SAL hybrid composite hydrogels containing 1.0% SAL and 1.0% BENT are 1017 - 1905 with the incorporation of SAL and BENT into AAm/KSM hydrogels, while S_{eq}% of AAm/BENT/SAL hybrid composite hydrogels is 718 (**Table 1**). **Table 1** show that the value of S_{eq}% of the AAm/KSM/BENT/SAL hybrid composite hydrogels are 80% - 117% for water-60% of ACE, 62% - 79% for water-60% of MET, and 76% - 101% for water-60% of THF. The values of S_{eq}% of the hydrogels increased with the KSM content in the copolymers. S_{eq}% of AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT and AAm/KSM/BENT/SAL hybrid composite hydrogel systems are higher than S_{eq}% of AAm hydrogels [21] [24] [26]. In summary, we have observed the lower values of S_{eq}% in all solvent compositions in comparison with the values of S_{eq}% in water.

It was shown that a partially decrease of the values of S_{eq}% of AAm/KSM/SAL semi IPNs, AAm/KSM/BENT and AAm/KSM/BENT/SAL hybrid composite hydrogel systems when SAL and BENT have been added to the hydrogel systems [21]. Incorporation of SAL and BENT into the copolymer network leads to lower degrees of swelling. The reason of this may be due to the structures of SAL polymer and BENT, which form the crosslinked polymeric systems, instead of crosslinked AAm and KSM monomers. Thus the decrease of the value of S_{eq}%, is possible due to the decrease of partially hydrophilic character at crosslinked polymeric systems. However, there is no good relation between the values of S_{eq}% of the hydrogels, when SAL and/or BENT have been added to the polymeric systems [21]. The same characteristic swelling behavior and results could have been followed, if there have been investigated that the results of swelling studies of the hydrogels in binary mixtures of various compositions of water-solvent (ACE, MET and THF). Again here, it can be said that there was no good relation between the values of S_{eq}% of the hydrogels, when SAL and/or BENT have been added to the polymeric systems.

To understand the effect of KSM content on the swelling behavior in water in water-60% of ACE, in water-60% of MET, and in water-60% of THF, the values of S_{eq}% of the hydrogels versus the amounts of KSM were plotted in **Figures 3-6**. The values of S_{eq}% of the hydrogels gradually increased with increasing of KSM content in the hydrogels.

3.2. Equilibrium Water/Liquid Capacity

The water or liquid absorbed by AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels quantitatively represented by equilibrium water/liquid capacity (EWLC) also, and they can be calculated by the following equation [16] [21] [29] [30].

$$\text{EWLC} = \frac{m_{eq} - m_0}{m_{eq}} \tag{2}$$

Here, m_{eq} is the mass of the swollen gel at time t (equilibrium), and m_0 is the mass of the dry gel at time 0. The values of EWLC of the hydrogels were calculated.

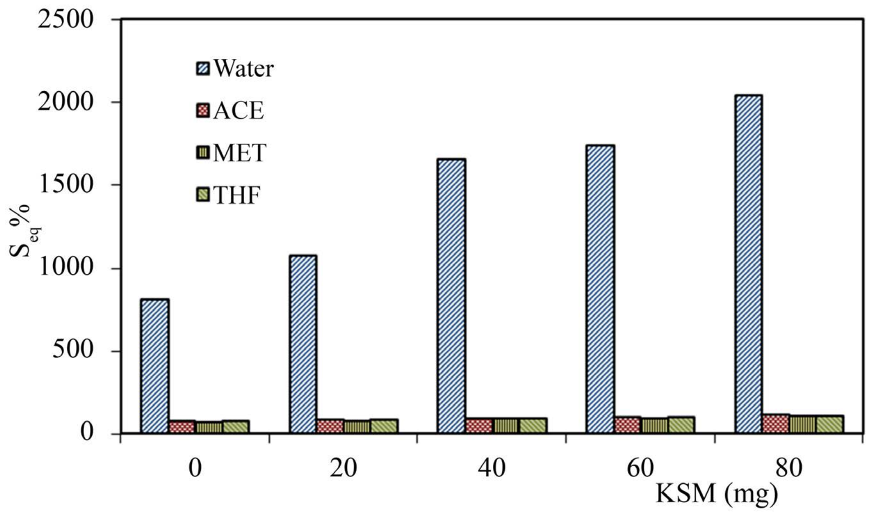


Figure 3. Effect of the content of KSM onto swelling of AAm/KSM hydrogels in water, in binary mixtures of water-60% of ACE, in water-60% of MET and in water-60% of THF.

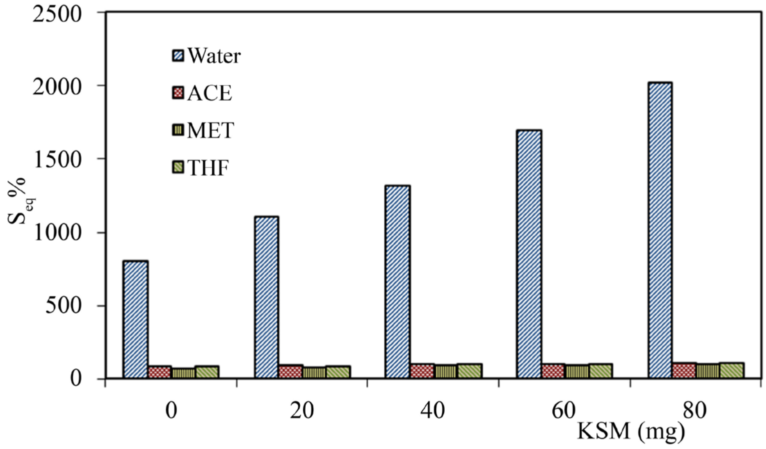


Figure 4. Effect of the content of KSM onto swelling of AAm/KSM/BENT hybrid hydrogels (containing of 1.0% BENT) in water, in binary mixtures of water-60% of ACE, in water-60% of MET and in water-60% of THF.

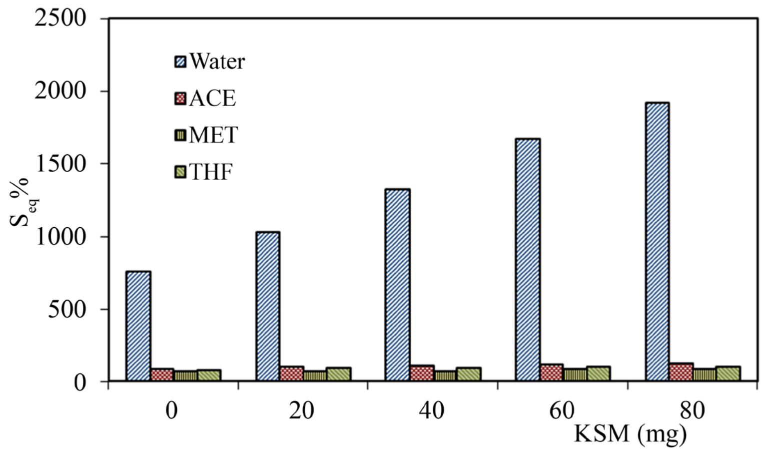


Figure 5. Effect of the content of KSM onto swelling of AAm/KSM/SAL semi IPN hydrogels (containing of 1.0% SAL) in water, in binary mixtures of water-60% of ACE, in water-60% of MET and in water-60% of THF.

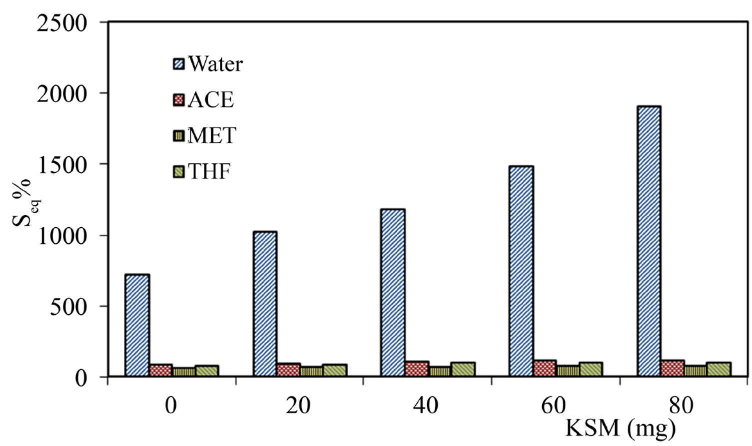


Figure 6. Effect of the content of KSM onto swelling of AAm/KSM/SAL/BENT biohybrid hydrogels (containing of 1.0% SAL and 1.0% BENT) in water, in binary mixtures of water-60% of ACE, in water-60% of MET and in water-60% of THF.

These values of EWLC of the hydrogels are tabulated in **Table 2**, which ranged between 0.3830 - 0.9527. The higher KSM, the more increase in EWLC was observed. Here, the main effect is the hydrophilic character of KSM groups. But, it has been seen a decreasing of the values of EWLC, if it has been investigated the values of EWLC of the hydrogels in binary mixtures of various compositions of water-solvent (ACE, MET and THF. The values range between 0.3830 - 0.5401. But, there is a partially decreasing of the values of EWLC is observed if SAL and BENT have been added to the hydrogel systems. Again here, it can be said that there was no good relation between the values of EWLC of the hydrogels, when SAL and/or BENT have been added to the hydrogels. Here, the main effect is the hydrophilic character of KSM monomer and non-hydrophilic character of the solvents as mentioned before then.

3.3. Diffusion

Analysis of the mechanisms of water or water-solvent binary mixtures diffusion into swellable polymeric systems has received considerable attention in recent

Table 2. The values of EWLC in water or binary mixture of water-solvent (ACE, MET and THF).

KSM/mg	0	20	40	60	80
	Equilibrium water/liquid capacity (EWLC)				
	Water				
AAm/KSM	0.8899	0.9148	0.9314	0.9455	0.9533
AAm/KSM/BENT	0.8891	0.9169	0.9293	0.9441	0.9527
AAm/KSM/SAL	0.8835	0.9115	0.9297	0.9437	0.9504
AAm/KSM/BENT/SAL	0.8778	0.9105	0.9218	0.9367	0.9501
	Water-60% of ACE				
AAm/KSM	0.4315	0.4563	0.4801	0.4981	0.5272
AAm/KSM/BENT	0.4504	0.4740	0.4914	0.5030	0.5112
AAm/KSM/SAL	0.4494	0.4984	0.5216	0.5293	0.5227
AAm/KSM/BENT/SAL	0.4459	0.4767	0.5166	0.5290	0.5401
	Water-60% of MET				
AAm/KSM	0.4054	0.4410	0.4716	0.4834	0.5135
AAm/KSM/BENT	0.4000	0.4591	0.4708	0.4786	0.4930
AAm/KSM/SAL	0.3958	0.4088	0.4155	0.4490	0.4570
AAm/KSM/BENT/SAL	0.3830	0.4036	0.4179	0.4273	0.4427
	Water-60% of THF				
AAm/KSM	0.4208	0.4492	0.4840	0.4940	0.5193
AAm/KSM/BENT	0.4461	0.4583	0.4884	0.4945	0.5167
AAm/KSM/SAL	0.4276	0.4712	0.5044	0.4889	0.4993
AAm/KSM/BENT/SAL	0.4320	0.4677	0.4710	0.4859	0.5015

years, because of important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural processing. The following equation is used to determine the nature of diffusion of water or water-solvent mixtures into hydrogels [21] [24] [25] [26] [30].

$$F = \frac{M_t}{M_s} = kt^n \tag{3}$$

Here, F is the fractional uptake at time t; M_t and M_s are the mass uptake of the water or water-solvent mixtures at time t and the equilibrium, respectively. Here, (n) is diffusion exponent, and (k) is diffusion constant. Equation (3) is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II transport are defined by n values of 0.5 and 1.0, respectively [21] [24] [25] [26] [30] [31] [32]. The n value of anomalous transport behavior (non-Fickian diffusion) is between Fickian and Case II. The values of n and k were calculated from the slope and the intercept of the plot of $\ln F$ against $\ln t$, respectively.

For chemically crosslinked highly swollen AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels, the plots of lnF vs. lnt where F is equal to (M_t/M_s) are shown in **Figure 7** for AAm/KSM/BENT hybrid hydrogels in water-60% of ACE, as representative. Diffusional exponents (n) and diffusion constant (k) are calculated from the slopes and intercepts of the lines, respectively, and are listed in **Tables 3-5**.

Tables 3-5 show that the values of the number determining the type of diffusion (n) are between 0.426 - 1.056. Hence the diffusion of binary mixtures of water-solvent (60% of solvent (ACE, MET and THF) of various compositions into the hydrogel systems is generally found to have a non-Fickian character. When the diffusion type is anomalous behavior, the relaxation and diffusion

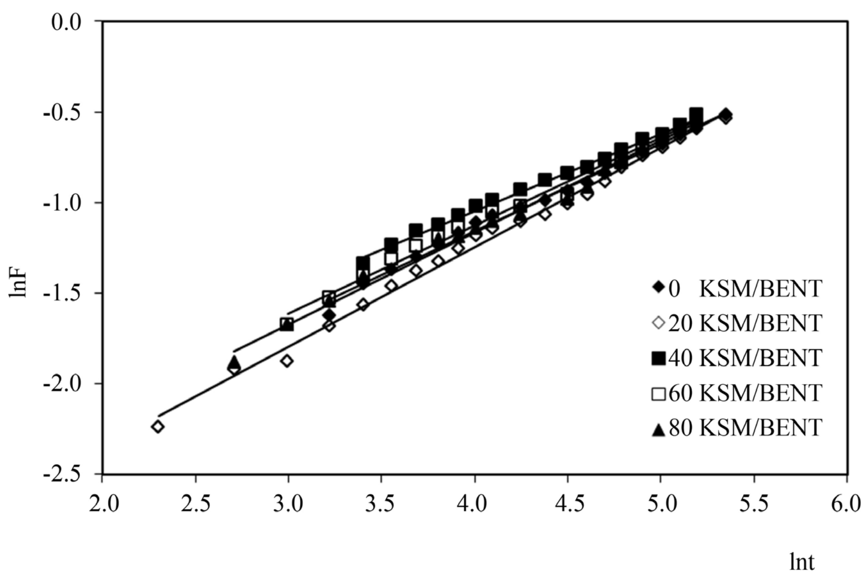


Figure 7. Plots of $\ln F$ versus $\ln t$ for AAm/KSM/BENT biohybrid hydrogels in binary mixture water-60% of ACE.

Table 3. Some diffusion parameters of the hydrogels in binary mixture of water-60% of ACE.

KSM/mg	0	20	40	60	80
			Water-60% of ACE		
			Diffusion exponent (n)		
AAm/KSM	0.645	0.649	0.734	0.577	0.612
AAm/KSM/BENT	0.484	0.549	0.426	0.486	0.506
AAm/KSM/SAL	0.692	0.662	0.668	0.758	0.731
AAm/KSM/BENT/SAL	0.629	0.682	0.741	0.812	0.794
			Diffusion constant ($k \times 10^3$)		
AAm/KSM	20.99	20.14	12.02	27.18	22.21
AAm/KSM/BENT	45.18	31.97	64.01	46.32	41.11
AAm/KSM/SAL	19.45	20.82	20.38	14.47	16.03
AAm/KSM/BENT/SAL	22.39	17.89	15.14	10.79	11.48
			Diffusion coefficient ($D \times 10^5$)		
AAm/KSM	18.67	16.42	23.39	11.83	16.32
AAm/KSM/BENT	3.66	6.69	3.07	5.95	7.60
AAm/KSM/SAL	15.10	13.65	16.33	30.13	33.49
AAm/KSM/BENT/SAL	7.41	11.84	20.69	30.17	31.46
			Water/liquid sorption rate constant ($K_{sr} \times 10^3$)		
AAm/KSM	4.47	4.30	3.82	4.03	4.02
AAm/KSM/BENT	3.56	3.76	3.69	4.02	4.06
AAm/KSM/SAL	5.21	4.80	4.74	5.46	5.45
AAm/KSM/BENT/SAL	3.88	4.85	5.38	5.47	5.36

Table 4. Some diffusion parameters of the hydrogels in binary mixture of water-60% of MET.

KSM/mg	0	20	40	60	80
			Water-60% of MET		
			Diffusion exponent (n)		
AAm/KSM	0.561	0.634	0.648	0.644	0.673
AAm/KSM/BENT	0.584	0.654	0.677	0.667	0.713
AAm/KSM/SAL	0.693	0.704	0.719	0.745	0.684
AAm/KSM/BENT/SAL	0.745	0.721	0.725	0.693	0.679
			Diffusion constant ($k \times 10^3$)		
AAm/KSM	29.84	21.58	20.06	19.93	19.71
AAm/KSM/BENT	26.57	19.60	16.59	18.38	16.59
AAm/KSM/SAL	17.66	15.04	14.54	12.28	15.94
AAm/KSM/BENT/SAL	14.51	14.90	13.33	15.09	16.51

Continued

	Diffusion coefficient (D × 10^5)				
AAm/KSM	6.23	11.72	14.27	15.10	23.76
AAm/KSM/BENT	5.30	9.79	11.78	13.90	23.10
AAm/KSM/SAL	11.40	12.39	15.71	18.83	15.63
AAm/KSM/BENT/SAL	10.44	10.26	10.89	10.67	11.91
	Water/liquid sorption rate constant (K_{sr} × 10^3)				
AAm/KSM	3.69	3.91	4.06	3.86	4.75
AAm/KSM/BENT	3.79	4.08	3.90	4.08	4.98
AAm/KSM/SAL	5.14	4.51	4.67	4.28	3.97
AAm/KSM/BENT/SAL	5.57	4.96	4.18	3.99	3.92

Table 5. Some diffusion parameters of the hydrogels in binary mixture of wateer-60% of THF.

KSM/mg	0	20	40	60	80
	Water-60% of THF				
	Diffusion exponent (n)				
AAm/KSM	0.648	0.910	0.835	0.857	0.843
AAm/KSM/BENT	0.499	0.611	0.449	0.534	0.555
AAm/KSM/SAL	0.768	0.732	0.902	0.907	0.694
AAm/KSM/BENT/SAL	0.678	0.877	0.845	1.056	1.038
	Diffusion constant (k × 10^3)				
AAm/KSM	19.74	4.91	7.10	6.02	6.66
AAm/KSM/BENT	40.54	21.87	56.03	34.41	31.44
AAm/KSM/SAL	12.27	13.42	5.76	5.14	13.65
AAm/KSM/BENT/SAL	19.04	6.41	6.40	3.67	5.04
	Diffusion coefficient (D × 10^5)				
AAm/KSM	12.17	31.95	28.84	32.64	35.97
AAm/KSM/BENT	3.94	8.81	3.77	7.73	10.30
AAm/KSM/SAL	17.74	16.14	31.32	32.78	15.95
AAm/KSM/BENT/SAL	10.61	21.71	19.05	58.85	81.03
	Water/liquid sorption rate constant (K_{sr} × 10^3)				
AAm/KSM	4.32	4.09	3.92	3.85	3.85
AAm/KSM/BENT	4.12	3.70	4.64	4.32	4.31
AAm/KSM/SAL	5.06	4.60	4.67	4.25	3.37
AAm/KSM/BENT/SAL	4.99	4.83	3.67	7.34	8.55

time are of the same order of magnitude [31] [32]. **Tables 3-5** show that the number determining the type of diffusion (n) is over 0.50 in general. Hence the diffusion of water or water-solvent mixtures into the hydrogels is determined to be a non-Fickian character [31] [32]. When the diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude [31] [32].

The study of diffusion phenomena of water or water-solvent binary mixtures in hydrogels is of value in that it clarifies polymer behavior. For hydrogel characterization, the diffusion coefficients can be calculated by various methods. The diffusion coefficient, D of the water or water-solvent mixtures was calculated using the following equation [33] [34].

$$\mathrm{D} = \pi r^2 \left(\frac{k}{4}\right)^{1/n} \tag{4}$$

Here D is in $cm^2 \cdot s^{-1}$, r is the radius of a cylindrical polymer sample, n is the diffusional exponent and k is a constant incorporating characteristic of the macromolecular network system and the penetrant. The values of diffusion coefficient determined for the hydrogels are listed in **Tables 3-5**. **Tables 3-5** show that the values of the diffusion coefficient of AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels vary from 3.66×10^{-5} $cm^2 \cdot min^{-1}$ to 81.03×10^{-5} $cm^2 \cdot min^{-1}$ for binary mixtures of water-solvent (60% of ACE, 60% of MET and 60% of THF). But, the values of the diffusion coefficient of AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels vary from 35.44×10^{-5} $cm^2 \cdot min^{-1}$ to 118.28×10^{-5} $cm^2 \cdot min^{-1}$ for water [21]. It can be said that there is no good relation between the values of the diffusion coefficient of AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid hydrogels, and AAm/KSM/BENT/SAL biohybrid hydrogels for binary mixtures of water-solvent (60% of ACE, 60% of MET and 60% of THF).

3.4. Water/Liquid Sorption Rate

Other important diffusion parameter can be "water/liquid sorption rate constant" (K_{sr}). This parameter can be calculated by the equation below [21] [35].

$$-\ln(1-F) = K_{sr}t + E \tag{5}$$

where t is sorption time, "K_{sr}" is water/liquid sorption rate constant, F (described previously), and E are constants. For AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels, the plots for their $-\ln(1-F)$ *vs* t are shown in **Figure 8** (an representative for for AAm/KSM/SAL semi IPN hydrogels in water-60% of MET).

The values of K_{sr} of the AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels calculated from the slope of the plots are tabulated in **Tables 3-5**. The ranges vary, from 3.37×10^{-3} min^{-1} to 8.55×10^{-3} min^{-1}. The

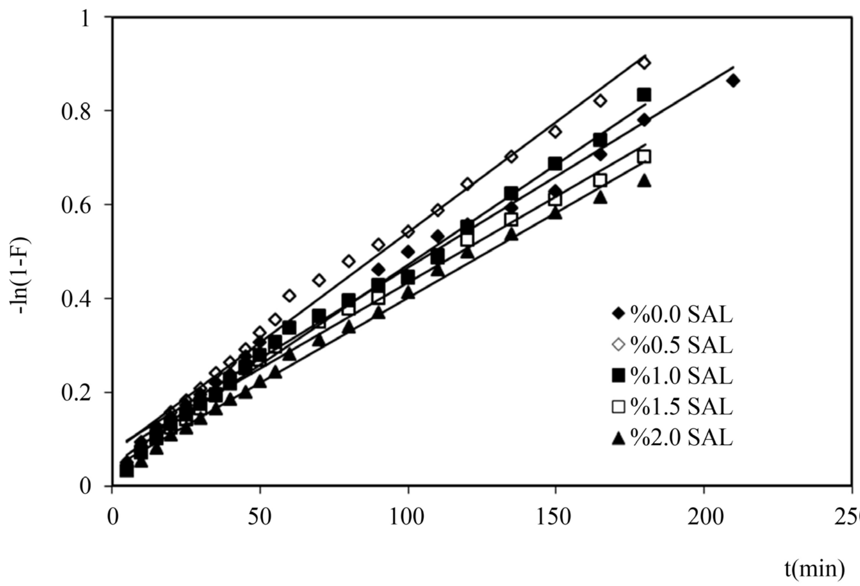


Figure 8. Plots of –ln(1 – *F*) versus lnt for AAm/KSM/SAL semi IPN hydrogels in binary mixture water-60% of MET.

values of the values of K_{sr} of the AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels vary from 4.28×10^{-3} min^{-1} to 10.50×10^{-3} min^{-1} for water [21].

Tables 3-5 showed that The values of K_{sr} of the AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels are generally lower than that of AAm hydrogels, AAm/SAL semi IPNs, AAm/BENT hybrid hydrogels, and AAm/SAL/BENT biohybrid hydrogels for water-60% of ACE and water-60% of MET. The reason for this may be due to the hydrophilic and ionic characteristics of KSM. Water sorption into hydrogel may be irregular as the KSM molecules consists of many charged functional groups, which possibly leads to no good correlation between the values of K_{sr} of the AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels for water-60% of THF. For the reason of this, it can be said that the ring structure of the THF molecules. On the other hand, it can be said that more irregular forms could be occurred in cross-linked structure by adding of SAL and BENT.

3.5. SAL and BENT Effect on Swelling and Diffusion

For investigation of the effect of mass/content of SAL and BENT on the swelling and diffusional properties of AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels, the related swelling isotherms and related swelling kinetic curves of hydrogel systems were constructed for swelling of the hydrogels in binary mixtures of water-solvent. Effect of SAL and BENT on some swelling and diffusion parameters of AAm/KSM/SAL semi IPNs and AAm/KSM/BENT hybrid hydrogels having of 60 mg KSM with different volume (as mL) of 2.0% of BENT-water suspension or 2.0% of aqueous SAL solutions were tabulated in Table 6 and Table 7.

It was shown that an increasing of the values of S_{eq}% of AAm/KSM/SAL semi IPNs and AAm/KSM/BENT hybrid hydrogels having of 60 mg KSM with different SAL and different BENT contents, when SAL and BENT have been added

Table 6. Some swelling and diffusion parameters of AAm/KSM/BENT hybride hydrogels having of 60 mg of KSM with different BENT content.

2.0% of BENT-water suspension (mL)	0.25	0.50	0.75	1.00
		Water		
S_{eq}%	1775	1690	1934	1980
EWLC	0.9466	0.9441	0.9508	0.9519
n	0.619	0.594	0.633	0.631
$k \times 10^3$	24.13	27.98	21.28	21.39
$D \times 10^5$	29.58	42.12	48.61	50.46
$K_{sr} \times 10^3$	4.83	4.73	4.47	4.54
		Water-60% of ACE		
S_{eq}%	81	101	107	118
EWLC	0.4481	0.5030	0.5167	0.5422
n	0.5130	0.4866	0.5288	0.5012
$k \times 10^3$	41.30	46.32	36.94	41.64
$D \times 10^5$	6.75	5.95	9.03	8.70
$K_{sr} \times 10^3$	4.06	4.02	4.11	3.85
		Water-60% of MET		
S_{eq}%	73	92	95	103
EWLC	0.4207	0.4786	0.4818	0.5062
n	0.754	0.667	0.795	0.865
$k \times 10^3$	19.93	13.40	18.38	26.83
$D \times 10^5$	20.24	13.90	26.83	47.76
$K_{sr} \times 10^3$)	5.10	4.08	4.61	5.72
		Water-60% of THF		
S_{eq}%	78	98	101	100
EWLC	0.4208	0.4945	0.5025	0.5000
n	0.613	0.534	0.606	0.879
$k \times 10^3$	23.51	34.41	25.59	4.79
$D \times 10^5$	11.68	7.73	13.48	33.69
$K_{sr} \times 10^3$)	3.99	4.32	3.86	3.19

Table 7. Some swelling and diffusion parameters of AAm/KSM/SAL semi IPN hydrogels having of 60 mg of KSM with different SAL content.

2.0% of aq. SAL sol. (mL)	0.25	0.50	0.75	1.00
		Water		
S_{eq}%	1571	1677	1836	2055
EWLC	0.9402	0.9437	0.9483	0.9536
n	0.636	0.646	0.632	0.668
$k \times 10^3$	23.94	21.08	21.09	16.39
$D \times 10^5$	30.69	46.08	41.36	47.13
$K_{sr} \times 10^3$	5.62	4.91	4.38	4.24
		Water-60% of ACE		
S_{eq}%	101	112	121	128
EWLC	0.5015	0.5293	0.5485	0.5606
n	0.714	0.757	0.803	0.866
$k \times 10^3$	18.01	14.47	11.05	8.10
$D \times 10^5$	22.89	30.13	37.19	49.74
$K_{sr} \times 10^3$	5.66	5.46	5.45	5.68
		Water-60% of MET		
S_{eq}%	72	81	84	86
EWLC	0.4179	0.4490	0.4558	0.4630
n	0.668	0.745	0.668	0.728
$k \times 10^3$	19.93	19.52	12.28	16.17
$D \times 10^5$	13.93	18.83	13.25	17.67
$K_{sr} \times 10^3$	4.71	4.28	3.68	3.63
		Water-60% of THF		
S_{eq}%	93	96	98	110
EWLC	0.4831	0.4889	0.4939	0.5244
n	0.978	0.907	0.859	0.825
$k \times 10^3$	4.55	5.14	3.88	8.35
$D \times 10^5$	43.31	32.78	23.25	32.90
$K_{sr} \times 10^3$	5.56	4.25	2.87	4.47

to the hydrogel systems. Incorporation of SAL and BENT into the copolymer network leads to higher values of S_{eq}%. The reason of this increasing may be the polymeric structure and partially hydrophilic character of SAL and BENT. So, it was seen that increasing of the value of the S_{eq}%, because of increasing of hydrophilic character at cross-linked polymeric systems. On the other hand, again it can be seen that similar characteristic behavior on the other some swelling and diffusion parameters, if **Table 6** & **Table 7** have been investigated.

3.6. Effect of Solvent on Swelling and Diffusion

Swelling of AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels in binary mixtures of water-solvent may be evaluated by the composition of solvent. Variations of the S_{eq}% of the hydrogels as a function of the solvent contents/concentration in the binary mixtures of water-solvent have been plotted in **Figures 9-12**. The values of some swelling and diffusion parameters of AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels in water or binary mixture of water-solvent (ACE, MET and THF) were tabulated in **Tables 8-11**.

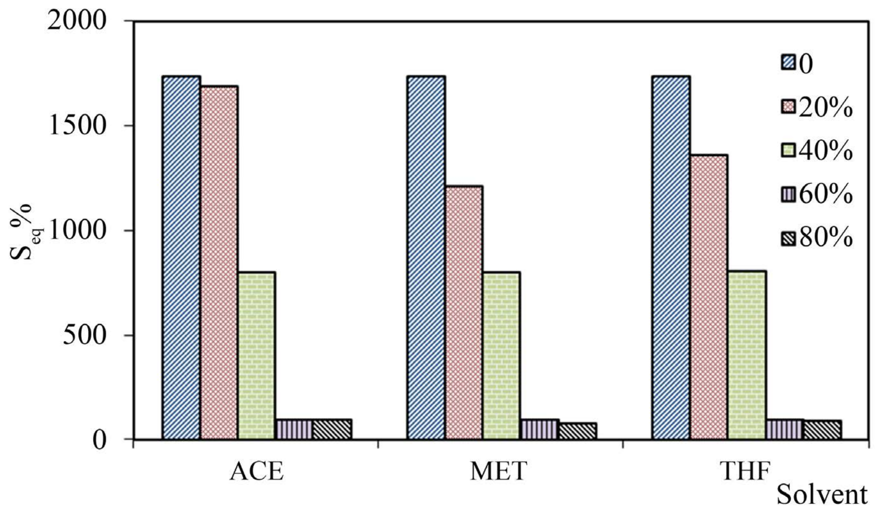


Figure 9. Variation of the equilibrium percentage swelling ratio (S_{eq}) of AAm/KSM hydrogels as a function of the solvent composition in the binary mixtures of water-solvent.

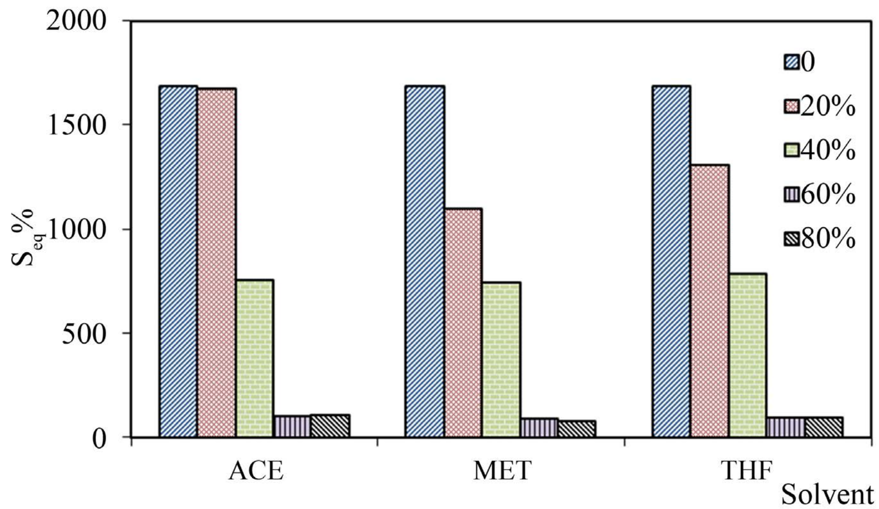


Figure 10. Variation of the equilibrium percentage swelling ratio (S_{eq}) of AAm/KSM/BENT hybrid hydrogels as a function of the solvent composition in the binary mixtures of water-solvent.

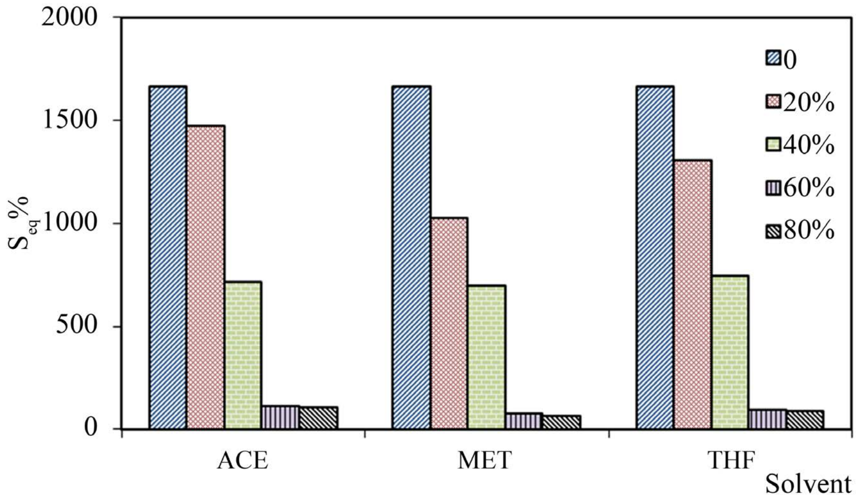


Figure 11. Variation of the equilibrium percentage swelling ratio (S_{eq}) of AAm/KSM/SAL semi IPN hydrogels as a function of the solvent composition in the binary mixtures of water-solvent.

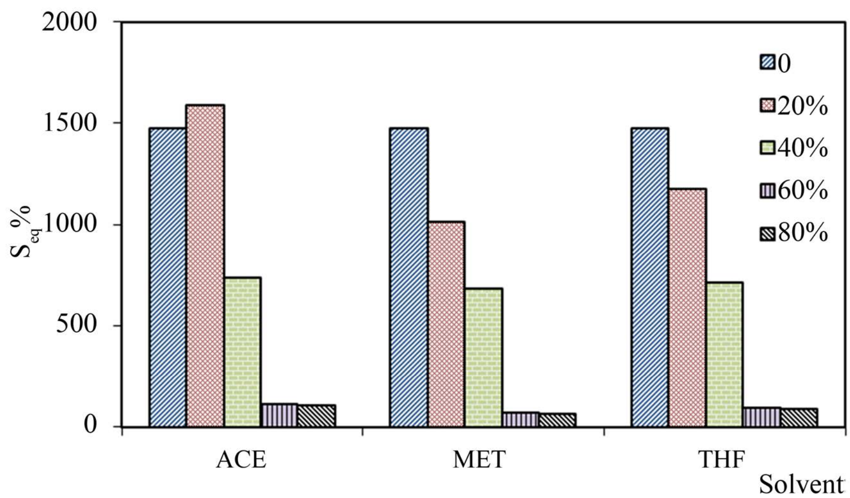


Figure 12. Variation of the equilibrium percentage swelling ratio (S_{eq}) of AAm/KSM/SAL/BENT biohybrid hydrogels as a function of the solvent composition in the binary mixtures of water-solvent.

Table 8. The values of some swelling and diffusion parameters of AAm/KSM hydrogels in water or binary mixture of water-solvent (ACE, MET and THF).

Percentage of solvent.	water	20%	40%	60%	80%
			ACE		
S_{eq}%	1735	1690	802	99	97
EWLC	0.9455	0.9441	0.8891	0.4981	0.4914
n	0.699	0.594	0.750	0.573	0.426
$k \times 10^3$	18.10	27.98	17.18	27.18	64.01
D $\times 10^5$	101.18	42.12	66.60	11.83	3.07
$K_{sr} \times 10^3$	4.60	4.75	7.31	4.03	3.73

Continued

			MET		
S_{eq}%	1735	1212	803	94	78
EWLC	0.9455	0.9238	0.8892	0.4834	0.4393
n	0.699	0.709	0.836	0.644	0.847
$k \times 10^3$	18.10	13.60	10.78	19.93	6.38
$D \times 10^5$	101.18	43.84	80.38	15.10	22.13
$K_{sr} \times 10^3$	4.60	3.93	6.45	3.86	2.40
			THF		
S_{eq}%	1735	1361	804	98	89
EWLC	0.9455	0.9316	0.8873	0.4940	0.4715
n	0.699	0.707	0.745	0.970	0.847
$k \times 10^3$	18.10	18.34	15.46	3.58	6.38
$D \times 10^5$	101.18	76.22	54.92	45.99	22.13
$K_{sr} \times 10^3$	4.60	6.24	6.17	3.87	3.86

Table 9. The values of some swelling and diffusion parameters of AAm/KSM/BENT hybride hydrogels in water or binary mixture of water-solvent (ACE, MET and THF).

Percentage of solvent.	water	20%	40%	60%	80%
			ACE		
S_{eq}%	1690	1678	757	101	108
EWLC	0.9441	0.9437	0.8833	0.5030	0.5108
n	0.594	0.636	0.670	0.486	0.675
$k \times 10^3$	27.98	22.00	22.53	46.32	20.06
$D \times 10^5$	42.12	49.80	41.90	7.43	19.81
$K_{sr} \times 10^3$	4.73	4.91	6.20	4.02	4.90
			MET		
S_{eq}%	1690	1101	745	92	76
EWLC	0.9441	0.9168	0.8863	0.4786	0.4319
n	0.594	0.673	0.779	0.667	0.659
$k \times 10^3$	27.98	21.09	16.42	18.38	22.14
$D \times 10^5$	42.12	50.84	82.76	15.82	14.51
$K_{sr} \times 10^3$	4.73	5.76	8.05	4.08	4.59
			THF		
S_{eq}%	1690	1312	788	98	95
EWLC	0.9441	0.9292	0.8873	0.4945	0.4870
n	0.594	0.633	0.750	0.494	0.487
$k \times 10^3$	27.98	22.17	17.44	35.00	22.14
$D \times 10^5$	42.12	39.03	56.18	7.98	18.95
$K_{sr} \times 10^3$	4.73	4.71	7.34	4.26	4.59

Table 10. The values of some swelling and diffusion parameters of AAm/KSM/SAL semi IPN hydrogels in water or binary mixture of water-solvent (ACE, MET and THF).

Percentage of solvent.	water	20%	40%	60%	80%
			ACE		
S_{eq}%	1667	1475	716	112	107
EWLC	0.9437	0.9365	0.8774	0.5293	0.5159
n	0.646	0.624	0.693	0.757	0.740
$k \times 10^3$	21.08	26.87	28.04	14.47	15.14
$D \times 10^5$	46.08	47.66	67.65	30.13	20.69
$K_{sr} \times 10^3$	4.91	6.14	10.5	5.46	5.38
			MET		
S_{eq}%	1667	1025	701	81	69
EWLC	0.9437	0.9111	0.8752	0.4473	0.4071
n	0.646	0.674	0.875	0.745	0.707
$k \times 10^3$	21.08	19.06	9.96	12.28	15.10
$D \times 10^5$	46.08	40.84	67.74	18.83	12.47
$K_{sr} \times 10^3$	4.91	5.04	6.91	4.28	4.54
			THF		
S_{eq}%	1667	1310	746	96	93
EWLC	0.9437	0.9291	0.8818	0.4889	0.4818
n	0.646	0.642	0.670	0.907	0.902
$k \times 10^3$	21.08	20.34	22.83	5.14	5.79
$D \times 10^5$	46.08	38.58	31.92	32.78	35.87
$K_{sr} \times 10^3$	4.91	4.43	6.34	4.25	4.71

Table 11. The values of some swelling and diffusion parameters of AAm/KSM/SAL/BENT biohybride hydrogels in water or binary mixture of water-solvent (ACE, MET and THF).

Percentage of solvent.	water	20%	40%	60%	80%
			ACE		
S_{eq}%	1479	1589	740	112	107
EWLC	0.9367	0.9408	0.8809	0.5290	0.5160
n	0.641	0.650	0.640	0.763	0.528
$k \times 10^3$	27.08	22.58	22.53	13.31	36.94
$D \times 10^5$	59.28	53.53	34.62	25.09	5.46
$K_{sr} \times 10^3$	6.80	5.63	6.20	5.36	4.11
			MET		
S_{eq}%	1479	1017	684	75	68
EWLC	0.9367	0.9105	0.8745	0.4273	0.4054
n	0.641	0.628	0.657	0.763	0.589

Continued

$k \times 10^3$	27.08	28.06	30.43	13.31	28.92
$D \times 10^5$	59.28	39.00	33.82	21.85	7.75
$K_{sr} \times 10^3$	6.80	6.19	7.93	3.99	5.14
			THF		
$S_{eq}\%$	1479	1179	712	95	89
EWLC	0.9367	0.9218	0.8768	0.4859	0.4711
n	0.641	0.636	0.710	0.763	0.845
$k \times 10^3$	27.08	25.57	26.15	13.31	6.38
$D \times 10^5$	59.28	47.20	53.72	25.09	18.97
$K_{sr} \times 10^3$	6.80	6.19	7.50	7.29	3.65

In **Tables 8-11**, the values of $S_{eq}\%$ of the hydrogels in binary mixture of water-solvent (ACE, MET and THF) are lower than the values of the hydrogels swollen in water. MET has got one alkyl group, but ACE and THF have got more than alkyl group from MET. With the increasing of alkyl group in the solvent, water diffusion can be affected by the structure of the organic molecules and the pores of hydrogels, hybrid composite hydrogels, and biohybrid composite hydrogels.

It was seen that decreasing of the values of $S_{eq}\%$ of the hydrogels with the increasing composition of the solvents. A possible reason is due to the hydrophobic character of the alkyl groups in the molecular structure, in which their hydrophobic character increases with the length of alky groups. For this reason, the more hydrophobic groups in the solvents get the less the swelling of the hydrogels in binary mixtures of water-solvent (in ACE, in MET and in THF). Again **Tables 8-11** show that the values of $S_{eq}\%$ for binary mixtures of 20%; 40%; 60%; and 80% of ACE are 1690% - 97%, for binary mixtures of 20%; 40%; 60%; and 80% of MET are 1212% - 68%, and for binary mixtures of 20%; 40%; 60%; and 80% of THF are 1361% - 89%.

For the swelling of AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels in binary mixtures of water-solvent (in ACE, in MET and in THF), it can be expected different behavior in water. This difference can be explained by the dependence of the ionization of the charged groups of the hydrogels in various compositions of binary mixtures of water-solvent. Because of the lower polarisability, higher hydrophobicity, and the lower hydrogen bonding occurring in swelling, the swelling value of the hydrogels can be lower than the swelling in water. Also for good description of content of KSM on swelling characterization, column plots of $S_{eq}\%$ versus various contents of KSM for AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels including of various contents of KSM could have been discussed here again

(**Figures 3-6**). It was seen that the values of S_{eq}% of the hydrogels increased with the KSM content in the crosslinked copolymers, again.

4. Conclusion

The present work has given the quantitative information on the swelling characteristic of AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels in water and in binary mixtures of water-solvent (in ACE, in MET and in THF). Generally, it was seen that swelling of AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels increased with the increasing of content of KSM. The hydrogels showed high water absorbency. The values of EWLC of the hydrogels in binary mixtures of various compositions of water-solvent (ACE, MET and THF) are changed between 0.3830 - 0.5401. They are changed between 0.3830 - 0.5401. Here, it was seen that there is no swelling in 100% composition of the solvents, such as ACE, MET and THF. The values of S_{eq}% of the hydrogels in water are higher than values of S_{eq}% of the hydrogels in organic solvents. It can be said that the more hydrophobic groups in binary mixtures of water-solvent get the less the swelling of the hydrogels. The main effect may be the non-hydrophilic character of alkyl groups in molecular structure of ACE, MET and THF. At the end of this study, it is seen that chemically crosslinked AAm/KSM hydrogels, AAm/KSM/SAL semi IPNs, AAm/KSM/BENT hybrid composite hydrogels and AAm/KSM/BENT/SAL biohybrid composite hydrogels may be used as a sorbent in binary mixtures of water-solvent, such as ACE, or MET, or THF. The utilization of these types of hydrogels in pharmaceuticals, agriculture, biotechnology, environment, sorption, separation, purification, water treatment process and other related area makes hydrogel more popular.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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