Obtaining and the Sorption Properties of Gel Compositions on the Basis of Acrylic Monomers and Bentonite Clay

M.A.Mahkamov[1]

M.G.Mukhamediev[1]

G.R.Otakuzieva[2]

A.S.Boymirzaev[2]

Abstract

Composite hydrogels (CH) on the basis of acrylic acid (AAc) and acrylamide (AA) with bentonite clay (BC) have been obtained. Kinetics of swelling of obtained CH in water were investigated and it was shown that it has a good swelling degree which was depended on the content of BC in CH. Sorption of methylene blue (MB) by gels from water solutions was investigated by static method. It was determined that the sorption ability of CH was higher as compare to the gels obtained without addition of BC. Influence of temperature on the sorption of MB from solutions was also investigated, which showed increased sorption of MB with rising the temperature of the medium. On the basis of obtained data, the changes of values of some thermodynamic parameters of the sorption process were calculated.

Key Word: Acrylic acid, acrylamide, bentonite clay, composite hydrogel, swelling, sorption

1. Introduction

The emergence of new fields of usage of polymeric hydrogels (PH) are put new demands to their properties. Recently, the need of usage of hydrogels has been increased due to their hydrophilic properties as well as other important characteristics such as high mechanical strength in hydrated state, high sorption capacity, etc. Combination in one material the indicated properties allow to make unique goods. For example, carriers of water insoluble medical drugs, sorbents which can absorb both hydrophilic and hydrophobic substances, new membrane materials and other objects [1-4]. Obtaining the compositions on the basis of cross-linking polymers by introducing different natural materials into the structure is one of the possible ways to solve this problem. In this respect, polymer-bentonite compositions have the special interest. High hydrophilic nature, good adsorption ability, low toxicity, and low cost are the reasons to choose the bentonite clay (BC) as a component to obtain polymeric compositions. Owing to these properties, BC has become perspective material for obtaining composites. In the literature [5-7], it was shown that particles of BC have provided to gels some new physicochemical properties and improved their mechanical characteristics. Therefore, construction of different composite hydrogels (CH) of the basis of polymer-BC and investigation of their physicochemical properties has a special interest both applied and scientific aspects.

[1] Department of Chemistry, National University of Uzbekistan, Tashkent 100174, Student city, Uzbekistan.
[2] Department of Chemical Technology, Namangan Institute of Engineering and Technology, 7 Kasansai str.,Namangan 160115, Uzbekistan

In this study, different CH compositions on the basis of acrylic acid (AAc) and acrylamide (AA) were obtained to investigate the effect of BC on the sorption characteristics of polymeric hydrogels (PH). The sorption of dye – methylene blue (MB) from water solutions of obtained PH was investigated.

2. Experimental

2.1. Chemicals

Acrylic acid (AAc; OAO Reactive, Russia) was vacuum distilled at 47°C/7 mmHg. Acrylamide (AA, Reanal, Hungary) was used without purification. The cross-linker N,N'-methylene-bisacrylamide (N,N'-MBAA; BDH Chemical Ltd, England) was of analytical grade. Methylene blue or methylthionimium chloride (MB, Russia) was pharmaceutical grade. Bentonite clay (Uzbekistan) of grade "Navbahor" was in following mass % compositions:

Name	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	FeO	others
Alkali bentonite clay	57,91	0,35	13,69	5,10	1,84	0,48	1,53	1,75	0,43	0,75	-	16,71

Before using, it was washed and dried on the air to constant mass and then was carefully reduced to fragments.

2.2. Synthesis of Hydrogels

PHs were obtained by polymerization of AAc and AA in water solution in the presence of cross-linking agent N,N'-MBAA. Oxidation-reduction system on the basis of H_2O_2 and $FeSO_4$ was used as initiator. Reaction was carried out at 298 K for 24 h. The obtained gels were placed in glass column and were washed by distillated water for 24 h, and then were dried at 318 K to constant mass.

2.3. Obtaining of Compositions

To obtain CH, first, the suspension of BC in water was prepared. For this, weighted amount of BC was added into water and the mixture was mixed on magnet stirrer for 2 h. Then, to the obtained suspension, the mixture of a monomer and cross-linking agent were added, and continued to mix again for 6 h. Further to the suspension were added the oxidation-reduction system and the mixture were poured in test-tubes. Compositions of obtained CHs are given in Table 1. Copolymerization was carried out for 20 h at 298 K. After polymerization gels were removed from test-tubes, were purified from residues of monomers by washing them in column with distillated water and were dried at 318 K to constant mass. The compositions of obtained gels are presented in Table 1.

Table 1. Conditions of Preparation of Composite Hydrogels on the Basis Aac-BC and AA-BC (In Terms of Mass to the Initial Mixture)

№ of sample	[AAc] or [AA] mass %	[BC],mass %	[AAc]:[BC] or [AA]:[BC] mass	[N,N'-МБАА], mass % from mass of AAc or AA
1	100	0	1:0	2
2	95	5	1:0,05	2
3	91	9	1:0,1	2
4	87	13	1:0,15	2
5	80	20	1:0,25	2
6	67	33	1:50	2
7	50	50	1:1	2
8	40	60	1:1,5	2
9	34	66	1:1,95	2

2.4. Degree of Swelling

Swelling degrees of PHs and CHs in water were determined by the gravimetric method in special cells supplied by net from nylon polymeric material. The values of the swelling degree of hydrogels (Q) were calculated by following formula:

$$Q = \frac{(M_s - M_d)}{M_d}$$

where, M_s and M_d are the masses of swelling and dry samples.

2.5. Sorption of Methylene Blue by Gels

Sorption of MB from water solutions of PHs and CHs was investigated by the spectrophotometric method. Samples of gels with equal masses were placed into water solutions of MB and their optical densities (D) were measured at 500 nm on SF-46 (Russia) after some intervals of time. Concentration of MB in solutions was determined on the basis of calibrated graphic.

3. Results and Discussion

3.1. Synthesis of Hydrogels and Their Rheological Characteristics

It is known that bentonites are minerals with high content of montmorillonite which form very small lamellar petaliform crystalline lattice able to expansion [8]. Its high exchange capacity in comparison with other clay minerals is explained by its crystals where exchange of ions takes place not only on the external surface of crystals but also in internal crystalline lattice between the atomic layers. Accordingly, at water sorption, the swelling takes place not only by the formation of solvating covers on the surface of particles but also by the introduction of water molecules between the crystalline lattice packets [9]. In the formation of polymeric compositions together with molecules of water molecules of monomers (AAc or AA) and cross-linking agent are also penetrated into the space between packages. Addition of initiator initiates the polymerization of monomers, with formation of nets filled with crystals of BC (figure 1). Such scheme of formation of polymeric compositions is presented in works [10, 11].

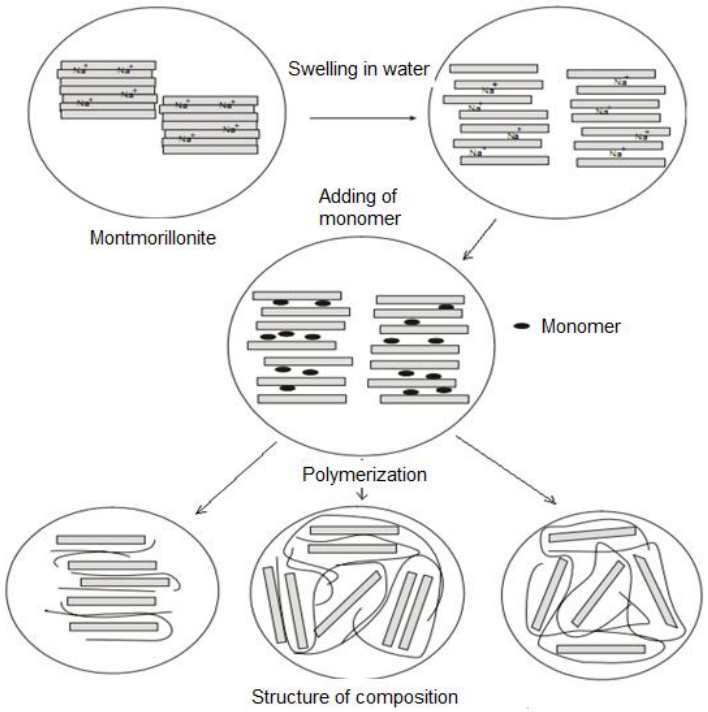

Figure1. Scheme of Formation of Chs on the Basis of Cross-Linking Aac (AA) and BC

Obtained in this work CHs are porous homogeneous mass well swelling in water. For the investigation of surface structures of obtained hydrogels their microphotographies have been taken which are presented in figure 2.

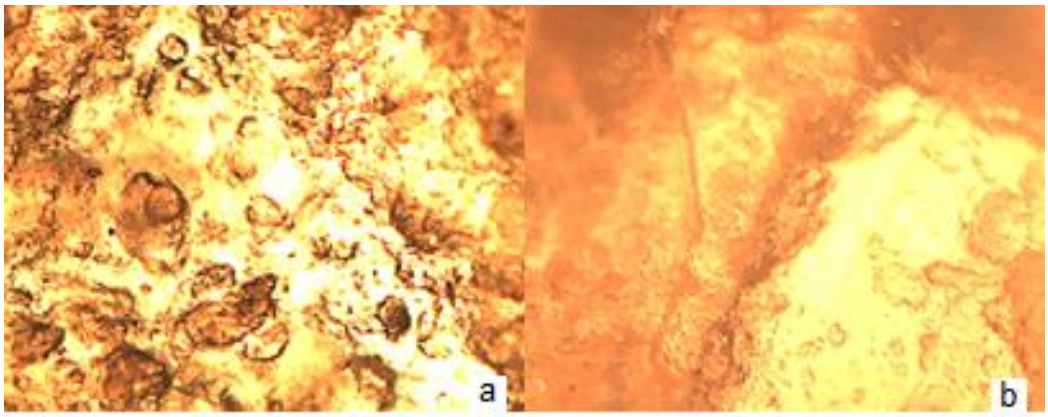

Figure 2. Microphotography of Cross-Linking Gels on the Basis of Aac-BC (A) And AA-BC (B) the Mass Content of BC in Compositions is 60 Mass %. 400-Fold Magnification

As shown from microphotographies of CH, the particles of BC in compositions practically don't change, indicating the destruction of packet structure of montmorillonite to smaller structures. It is also shown that the obtained CHs have homogeneous and porous structure.

3.2. Investigation of Swelling Kinetics of Obtained Gels in Water

Fig.3 presents swelling kinetics of PH on the basis of AAc, AA, and BC. As shown in the fig., gels obtained on the basis of AAc have highest swelling degree as compare to gels obtained on the basis of AA, though both were obtained in similar conductions. Samples of BC swell well in water too, the swelling degree of which has reached 8 g/g.

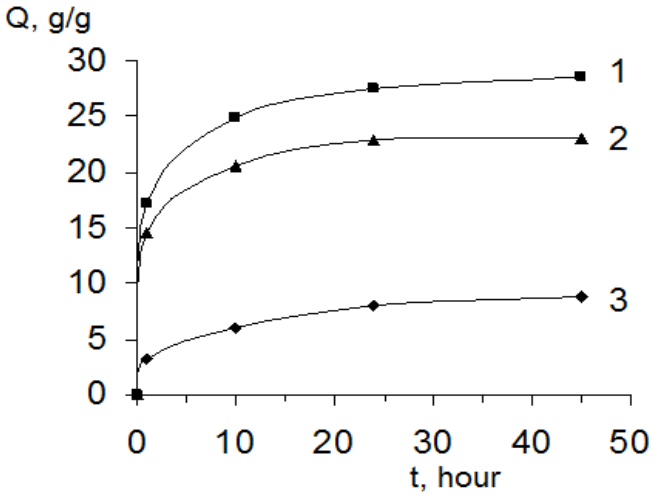

Figure 3. The Swelling Kinetics of the gels on the basis of AAc (1), AA (2), and BC (3) in Water. T=298 K

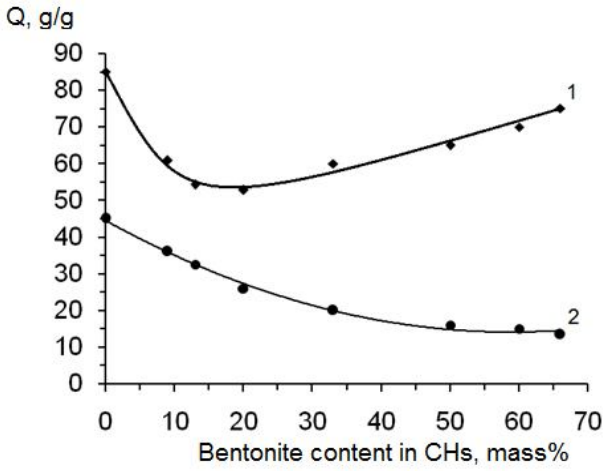

Figure 4. Dependence of Swelling degree of CH on the basis of AAc (1) and AA (2) Containing BC in their Compositions

Swelling investigations of CHs containing different amounts of BC has shown (fig.4.) that swelling kinetics for CHs on the basis of AAc and AA has different character. If in CHs on the basis of AA with increasing content of BC their degree of swelling in water has decreased gradually, but in case of CHs on the basis of AAc this dependence had an extreme character, i.e. with increasing of BC their swelling degree, first, sharply decreased and then gradually increased.

3.3. Sorption of Methylene blue by PH and CH from Water Solutions

Sorption of MB from water solutions of investigated gels was studied in static conditions. It was determined that at sorption of MB by dried sorption materials, in the beginning only sorption of water takes place, i.e. the process of swelling of gels and compositions occur. As a result, concentration MB in solution increases. Then after reaching of some swelling degree of PH and CH in water starts the sorption of MB by gels. In fig.5, the isotherms of sorption of MB by dried PHs on the basis of AAc, AA, and BC are presented.

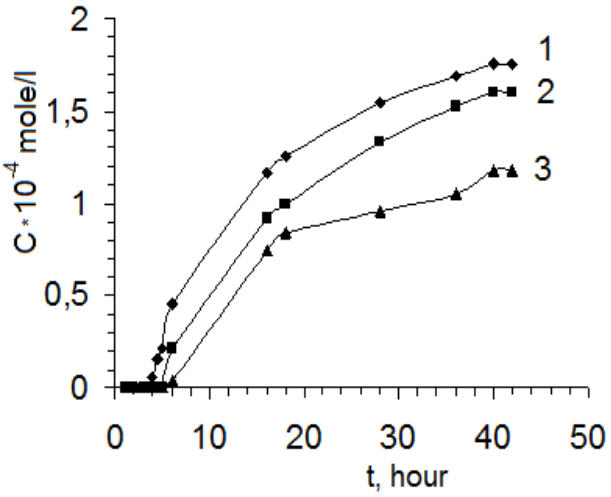

Figure 5. Sorption kinetics of MB from Solutions by gels on the basis of AAc (1), AA (2) and BC (3). Concentration of MB in water solution - $3*10^{-4}$ mol/l. T=293 K

Fig.5 shows that adsorption of MB by hydrogels on the basis of AAc, AA, and BC occurs spontaneously. In all cases, sorption of MB from water solutions occurred long time and the equilibrium was reached after 40 h. It is also shown that the sorption capacity of gels on the basis of AAc (fig.5, curve 1) is higher as compare to gels on the basis of AA and also BC.

In fig.6 the data obtained from the investigation of sorption of MB from CH solutions with different content of BC are presented.

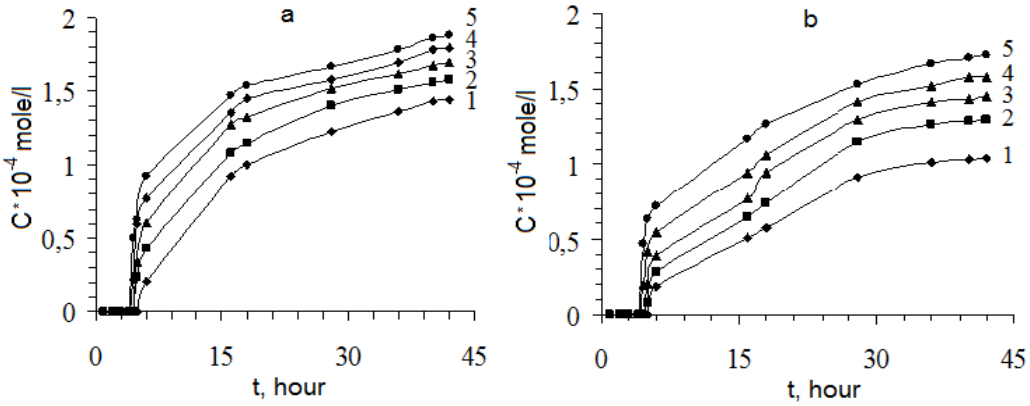

Figure 6. Kinetics of MB Sorption from Solutions of CH on the basis of AAc (a) and AA (b). 1,2,3,4,5 – CH with Content of BC in the Compositions of 0; 33; 50; 60; and 66 (mass %). Concentration of MB in Solution $2*10^{-4}$ mol/l. T=293 K

As it is shown in fig. 6, increasing the content of BC in CH increases their sorption capacity to MB. In Table 2 the values of C_{ads} (concentration of adsorbed MB) by sorbents are presented.

Table 2. Quantity of Adsorbed MB (C_{ads}) by the Samples of Sorbents from Water Solutions Concentration of MB in Solution is $2*10^{-4}$ mol/l. T=293 K

Sorbent	PH on the basis of AAc	PH on the basis of AA	C	CH on the basis of AAc (BC 66 mass %)	PH on the basis of AA (BC 66 mass %)
$C_{ads}*10^{-4}$ mol/l	1,43	1,03	0,75	1,88	1,72

Table 2 shows that the sorption ability of CHs is higher as compare to PHs and BCs. The addition of 66 mass % of BC into the gels leads to the increase of their sorption capacity from 31 to 67 % for AAc and AA, respectively.

In this work, the sorption of MB from water solutions by PHs and CHs at different temperatures was also investigated. The values of K (the constant of adsorption equilibrium) and Q_∞ (the capacity of adsorption monolayer) were calculated using the Langmuir isotherm which is presented in Table 3.

The Gibbs free energy was calculated using the equation of $\Delta G = -RT\ln K$ and the values of entropy (ΔS) and enthalpy (ΔH) changes were calculated using the equation of $\Delta G = \Delta H - T\Delta S$. All the calculated values of thermodynamical parameters of the sorption process of MB by gels are presented in Table 3.

Table 3. Thermodynamical Parameters of MB Sorption from Water Solutions by PHs and CHs on the basis of AAc and AA

Sorbent	T, K	$1/Q_\infty$ g/mol^{-1}	K, l/mol^{-1}	ΔGKj/mol	ΔHKj/mol	ΔSJ/mol·K
PH on the basis of AAc	298	512	807	-16,6	-29,0	-41.72
	303	421	928	-17,2		-38.95
	308	388	1090	-17,9		-36.06
PH on the basis of AAc	298	550	689	-16,2	-23,3	-24.05
	303	452	751	-16,7		-22.05
	308	394	1008	-17,7		-18.38
CH on the basis of AAc (BC 66 mass %)	298	268	1390	-17,9	-36,7	-62.97
	303	228	1568	-18,5		-59.86
	308	197	1955	-19,4		-56.06
CH on the basis of AA (BC 66 mass %)	298	326	1158	-17,5	-32,0	-48.77
	303	292	1290	-18,0		-46.08
	308	241	1740	-19,1		-41.97

Table 3 shows that the sorption of MB by the sorbents occurs with decreasing of ΔG, ΔH and ΔS of the system. Negative values of these parameters indicate that the sorption process is exothermic, occurs spontaneously, with compacting of the system due to the decrease of common numbers of particles because of the sorption of MB molecules by sorbents. Increasing the temperature leads to the increase of the maximum adsorption of MB by the sorbents and the equilibrium constant, indicating binding of dye by chemical adsorption.

Conclusions

In this work, CHs on the basis of AAc and AA were obtained with introduction of BC into their structures. It was shown that the obtained CHs are homogenous and have a porous structure with high hydrophility. Investigation of MB sorption of obtained CHs has shown that they have higher sorption capacity as compare to PH. This indicates that by the introduction of BC into the PH compositions allows to increase their sorption capacity and to decrease the content of synthetic polymers which is important from the ecological point of view. It was shown that increasing the temperature leads to the increase of MB sorption by gels, indicating on the chemical character of the process of binding. Thermodynamic parameters of the sorption process were calculated and were shown that it occurs with decreasing of ΔG, ΔH and ΔS of the system. This indicates that the sorption is an exothermic process and occurs spontaneously.

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