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Effect of montmorillonite on gelation and swelling behavior of sulfonated polyacrylamide nanocomposite hydrogels in electrolyte solutions

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ABSTRACT

Nanocomposite hydrogels were prepared by cross-linking of aqueous solutions of sulfonated polyacrylamide/sodium montmorillonite with chromium triacetate. The gelation process and effects of clay content and ionic strength on swelling behavior were investigated. X-ray diffraction patterns indicated that exfoliated type of microstructure was formed. Study of the gelation behavior using dynamic rheometery showed that the limiting storage modulus of the nanocomposite (NC) gels decreased with increasing clay content up to 1000 ppm, but it increased by further increase of Na^+-montmorillonite concentration. It was also found that with increasing the clay content, the viscous energy dissipation properties of the nanocomposite gels increased. The swelling ratio of nanocomposite gels in tap water decreased as the concentration of the clay increased. However, nanocomposite gels showed higher resistance against syneresis in electrolyte solutions as compared with unfilled gels. Therefore, they are potentially good candidates for enhanced oil recovery applications.

1. Introduction

Hydrophilic cross-linked polymer networks, i.e., hydrogels, are capable of absorbing and retaining large quantities of water. Because of their unique characteristics like hydrophilicity, swelling in aqueous media, and non-soluble nature in aqueous fluids, they are widely used in many applications such as hygiene, cosmetics, agriculture, medicine, biotechnology, and petroleum recovery treatments of mature reservoirs [1–5]. It has been found that increasing cross-linker concentration can enhance mechanical strength of hydrogels. However, a large amount of cross-linker could result in the reduction of swelling capability and mechanical toughness [6,7]. Recently, to overcome the weakness and limitations of the conventional hydrogels, preparation of nanocomposite hydrogels have attracted more attention [8–14]. These nanocomposite (NC) hydrogels have excellent properties, such as mechanical toughness, large deformability, high swelling/deswelling rates, and high transparency. These remarkable improvements in properties of nanocomposite hydrogels were ascribed to their characteristic network structure [9,15]. On the basis of the results of mechanical and swelling/deswelling properties of NC hydrogels, Haraguchi and Takehisa [11] proposed the existence of a unique organic/inorganic network structure for poly (*N*-isopropylamide) (PNIPA) – clay NC hydrogels. Their model is based on a uniform dispersion of exfoliated inorganic clay in an aqueous medium and PNIPA chains grafted on the clay surface at one or both ends. These NC gels mainly consist of polymer chains connecting neighboring clay sheets. In other words, polymer chains are effectively cross-linked by clay sheets. Also, because of the large distance between the clay sheets,

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all polymer chains in NC gels are long and flexible, adopting random conformations. Thus, the chain lengths between clay sheets may be proportional to the clay–clay interparticle distance and with a fairly narrow distribution of chain lengths. In contrast, polymer chains in ordinary gels are randomly cross-linked by a large number of organic cross-linking units and the chain lengths between cross-linking points are short on average and have a wide distribution of chain lengths between random cross-linking points. So because of this unique polymer/clay network structure in NC gels, they exhibit extraordinary mechanical, optical and swelling/deswelling properties [9,11].

Okay and Oppermann [8] prepared hydrogels by free-radical polymerization of acrylamide in aqueous clay dispersions and studied the structure of the resulting hydrogels using oscillatory deformation tests. Their rheological investigations revealed that there exists a fundamental difference, with regard to the viscous energy dissipating properties, between chemically cross-linked gels and those containing clay particles. They showed that the nanocomposite hydrogels exhibit a very strong dissipation mechanism compared to the chemically cross-linked gels, indicating that the dynamic adsorption/desorption equilibrium of the polyacrylamide chains with the particles dominates the elasticity of the gels.

While the preparation and properties of the composite and nanocomposite hydrogels synthesized by free-radical polymerization/gelation of the monomers in the presence of the clays with or without additional use of organic cross-linkers have been studied by various investigators [8–11,16–28], there are only a few reports about the preparation of NC hydrogels cross-linked by metallic cross-linkers in the presence of the clay [29,30].

In this research, novel nanocomposite hydrogels were prepared by cross-linking of aqueous solutions of sulfonated polyacrylamide/sodium montmorillonite with chromium triacetate. The rheological behavior, microstructure and influence of clay content and salt concentration on swelling behavior were studied. In addition, due to applications of the polyacrylamide gels in enhanced oil recovery (EOR) treatments for control of the excess water production through profile modification and blocking the paths with high permeability to water [31–34], swelling behaviors of the NC gels in the synthetic oil reservoir water were investigated.

2. Experimental

2.1. Materials

Sulfonated polyacrylamide (PAMPS) with an average molecular weight of 8×10^6, sulfonation degree of 25% and water content of less than 10 wt%, was provided by SNF Co., under the trade name of AN125. PAMPS is a copolymer of acrylamide and sodium salt of acrylamido propyl sulfonic acid (Fig. 1), which has higher thermal stability and salt resistance than standard hydrolyzed polyacrylamides and commercially it is used in enhanced oil recovery applications up to 120 °C. Chromium triacetate as a metallic cross-linker was purchased form Carlo Erba.

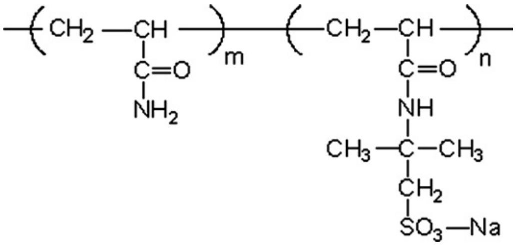

Fig. 1. PAMPS chemical structure.

Sodium montmorillonite hydrophilic clay (Na^+-MMT), under the commercial name of Cloisite Na^+, was provided by Southern Clay Products (SCP) Inc. The cation exchange capacity (CEC) and specific gravity of clay were 92.6 meq/100 g and 2.86 g/cc, respectively. 90 vol% of its dry powder has particle size less than 13 μ, according to the manufacturer's information. Its general formula is $AlSi_2O_5(OH) \times H_2O$.

2.2. Hydrogels preparation

The conventional and nanocomposite hydrogels were prepared according to the following steps. At first, the polymer solutions were prepared by gradual addition of the PAMPS powder to tap water while stirring to obtain clear viscous solutions. Dispersions of Na^+-MMT clay were prepared by stirring of its powder in tap water for 2 days. Then, separately prepared clay/water dispersions were added to PAMPS solutions while stirring at room temperature for 1 h. Cross-linking of the prepared solutions containing given amounts of PAMPS and clay was performed by adding of chromium triacetate/water solution and then stirring of the aqueous reaction mixtures (gelant solutions) at 75 °C using an overhead electronic stirrer (Heidolph PZR 2102) for 60–70 min. The products were immersed in an excess of tap water for 7 days to remove the residual uncross-linked polymers and impurities. For dewatering, ethanol (150 ml) was added to the gelled product for 24 h, after which the product was poured into Petri dishes and dried at 45 °C for 72–96 h in a vacuum-oven. The dried products were stored away from moisture, heat and light for further investigations. The detailed compositions of the prepared gels are listed in Table 1.

2.3. Characterization

To evaluate the dispersion of the clay in wet NC hydrogels, X-ray diffraction (XRD) was performed with a Philips Analytical X-ray using nickel-filtered Cu-Kα radiation ($\lambda = 0.154$ nm) under a voltage of 40 kV and a current of 25 mA. The XRD patterns were recorded with a step size of 0.05° from $2\theta = 1$ to 15°.

The average particle size of clay mineral in PAMPS solutions before cross-linking was determined at room temperature as a function of clay/polymer ratio by dynamic light scattering (DLS) method at wavelength λ of 532 nm using a Malvern NANO-ZS Zetasizer (Malvern Instruments, England). The scattering angle was fixed to be 173°. The samples for the DLS measurements were prepared by adding

Table 1
Formulations of the prepared nanocomposite gels

Sample code	Polymer concentration (ppm)	Cross-linker concentration (ppm)	Nanoclay concentration (ppm)
SG0	5000	500	–
SG1	5000	500	250
SG2	5000	500	500
SG3	5000	500	1000
SG4	5000	500	1500
SG5	5000	500	2000
SG6	5000	500	2500
SG7	5000	500	3000
SG8	5000	500	4000
SG9	5000	750	500
SG10	5000	300	500

of clay/water dispersions to PAMPS solutions while stirring at room temperature for 1 h.

To measure the equilibrium swelling ratios, tea bags (i.e., a 100 mesh nylon screen) containing pre-weighed dry samples were immersed entirely in tap and synthetic oil reservoir water (with the composition given in Table 2) and in 0.05, 0.15 and 0.5 M NaCl and $CaCl_2$ solutions and allowed to soak for 10 days to reach equilibrium state. The equilibrated swollen gels were allowed to drain by removing the teabags from the water and the excess surface water was removed with filter paper. The equilibrium swelling ratio (ESR) was measured using the following equation:

$$\mathrm{ESR} = \frac{W_s - W_o}{W_o} \tag{1}$$

where W_o and W_s are the weights of the dry and swollen gel, respectively.

The salt sensitivity factor (f) for each gel in oil reservoir water and electrolyte solutions was calculated from the following equation:

$$f = 1 - (\mathrm{ESR_e}/\mathrm{ESR}) \tag{2}$$

where ESR and $\mathrm{ESR_e}$ are the equilibrium swelling ratios of each gel in tap water and electrolyte media, respectively.

The viscoelastic properties of the NC gels were evaluated using a concentric cylinder physica MCR 300 dynamic Rheometer (Anton Paar) equipped with a Peltier device for temperature control. To carry out the rheological tests, the system was first heated to 75 °C, and then the aqueous reaction mixtures containing given amounts of PAMPS, clay and chromium triacetate (gelant solutions) were introduced into the heated cylinder and subjected to an oscillatory strain

$$\gamma(t) = \gamma_o \cos(\omega t) \tag{3}$$

and the shear stress was measured from the resultant torque

$$\sigma(t) = G^* \gamma_o \cos(\omega t + \delta) \tag{4}$$

Following equations were then used to calculate, the characteristic storage (G') and loss modulus (G'') from the complex modulus, G^*, and phase angle δ:

$$G' = G^* \cos\delta \tag{5}$$

$$G'' = G^* \sin\delta \tag{6}$$

$$G^* = G' + iG'' \tag{7}$$

A frequency of $\omega = 1$ Hz and a deformation amplitude $\gamma_o = 0.01$ were selected to ensure that the oscillatory deformation is within the linear regime. During all rheological tests, a thin layer of silicone oil was applied to the outer circular surface of the samples to prevent water loss.

Table 2
Composition of the tap and synthetic oil reservoir water

Ion concentrations (mg/L)		Ion type
Tap water	Synthetic oil reservoir water	
115	12800	Ca^{2+}
73	880	Mg^{2+}
300	61800	Na^+
6.1	810	K^+
542	63	HCO_3^-
395	142	SO_4^{2-}
276	156000	Cl^-

3. Results and discussion

3.1. Gelation process

The most widely used method for monitoring the gelation process and measuring the gel strength is viscosity measurement. However, this method has some obvious drawbacks. For example, the measured results are inaccurate and their repeatability is poor due to breakage and slipperiness of gel during the measurement. This method is especially unsuitable for a weak gel system because it can be broken easily and slides on rotator. Alternatively, the mechanical strength of a gel can be represented by its viscoelastic properties such as elastic module (G') and viscous module (G''). The distinct advantages of this method are that the gel structure will not be damaged during the measurement and that the data repeatability is satisfactory. In this research oscillatory time sweeps were performed by dynamic rheometry to monitor the in-situ gelation process of the aqueous reaction mixtures containing sulfonated polyacrylamide, cross-linker and clay (gelant solutions) and measuring the gel strength of the nanocomposite hydrogels. Fig. 2 compares the gelation behavior of the conventional and NC gels containing 1000 and 2000-ppm clay. Initially, G'' is larger than G', which is expected since the samples are still in the liquid state where viscous properties dominate, and therefore most (if not all) of the energy is lost as viscous heat. As the gelant begin to gel and a cross-linked network is formed, both G' and G'' begin to increase; however the rate of increase of G' is much higher than that of G'' since now the elastic properties of the gelling hydrogel begin to dominate. Consequently there is a crossover point where G' becomes larger than G''. The time required for this crossover is sometimes referred to as the gelation time [35]. The gelation process is assumed to be complete when G' and G'' reach a plateau value with time.

Fig. 3 shows the time sweep profiles of G' and G'' for the NC gels containing 0, 250, 500, 1000, 1500, 2000, 2500,

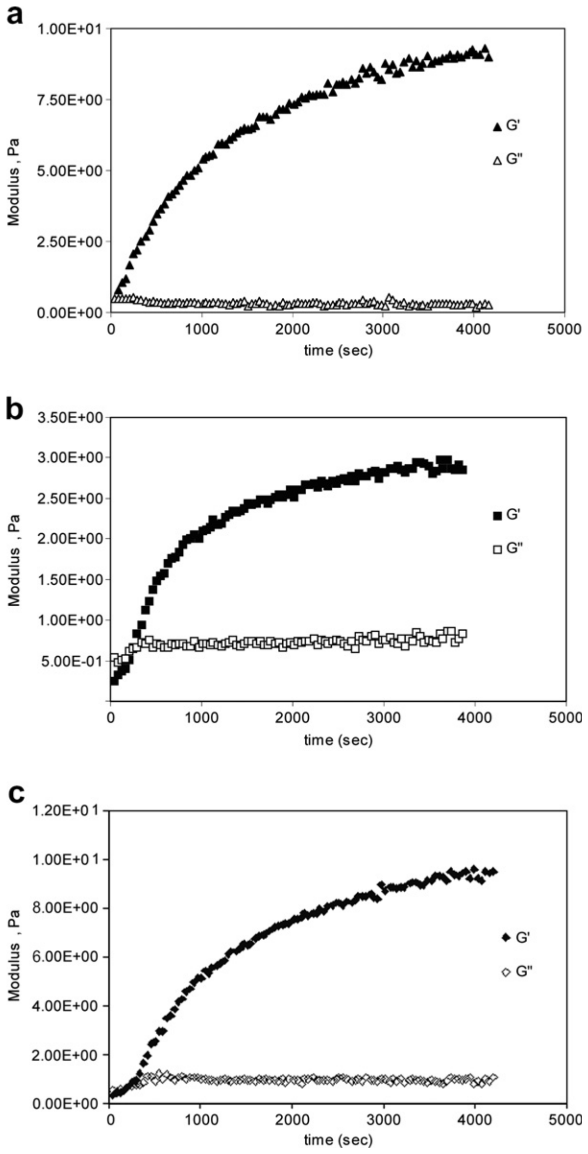

Fig. 2. Gelation process of (a) conventional PAMPS gel (b) NC gel with 1000 ppm clay and (c) NC gel with 2000 ppm clay (polymer concentration: 5000 ppm, cross-linker concentration: 500 ppm).

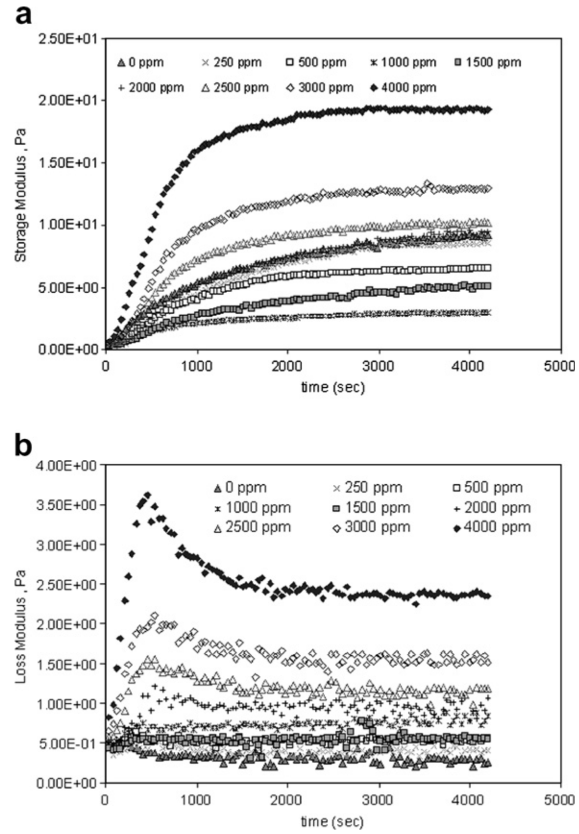

Fig. 3. Effect of clay concentration on time sweep profiles of (a) G' and (b) G'' (polymer concentration: 5000 ppm, cross-linker concentration: 500 ppm).

3000 and 4000 ppm clay. With or without the clay, the general trend is a rapid increase of the storage modulus followed by a plateau regime where the storage modulus slightly increases (Fig. 3a). The reaction period during which the G' rapidly increases corresponds to the regime of the sol–gel transition as well as the gel growth, while the slight increase corresponds to the post-cross-linking reactions in gel [8]. During the gelation of the sulfonated polyacrylamide in the presence of Na^+-MMT, G' increases rapidly and then approaches plateau value after about 3000 s.

Fig. 3b shows that the higher the clay content, the higher the loss modulus. Thus, addition of clay into the gelation system increases the viscous energy dissipating properties of the NC materials. Although the plot of G'' plateaus with time, it never decreases to zero, suggesting the viscoelastic nature of these hydrogels under the applied physical conditions. The slightly erratic nature of G'' observed during time sweep tests is attributed to grip–slip caused by the release of water from the hydrogels.

Fig. 4 shows the effect of clay content on the limiting storage modulus (G'_u) of the PAMPS NC gels. The limiting storage modulus of the NC gels decreases with increasing clay content up to 1000 ppm, which may be due to the partial adsorption of polymer chains onto the clay surface and/or ionic interactions between negative layers of sodium montmorillonite and Cr^{3+}. For Na^+-MMT loading greater than 1000 ppm, there is an increase in the limiting storage modulus of the NC gels. The increase in G' values at high clay concentration suggests the existence of strong interactions between polyacrylamide chains and clay, so that the nanoparticles are fixed in the gel network as additional effective junction points. According to the mechanism suggested by Haraguchi [7,9,11], the polyacrylamide chains are bound to the surface of the clay particles due to hydrogen bonds between the oxygen atoms of clay and the amide protons of the acrylamide as well as due to complex formation between the metal ions on the clay surface and the carbonyl oxygen of the acrylamide.

Another reason for increasing of G' values at high clay concentration may be the clay network formation as a

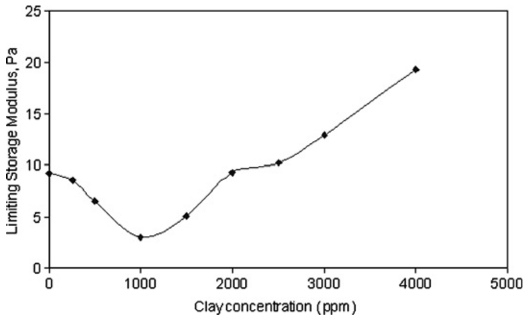

Fig. 4. Effect of clay concentration on limiting storage modulus (G'_u) of the PAMPS NC gels (polymer concentration: 5000 ppm, cross-linker concentration: 500 ppm).

result of significant clay layers interactions at high concentrations.

Fig. 5 shows the effect of the cross-linker concentration on gelation behavior of the NC gel containing 500 ppm clay. The higher the cross-linker content, the higher the elastic modulus, but the lower the loss modulus. Thus, increasing the cross-linker concentration of the gelation system decreases the viscous energy dissipating properties of the NC materials. Furthermore, it can be seen that with increased cross-linker concentration, the gelation point appears sooner. Thus, indicating that Cr^{3+} cross-linking of polyacrylamide is the rate-limiting reaction.

The loss factor $\tan\delta = G''/G'$ for each PAMPS/clay/cross-linker system was calculated from the limiting values of G' and G'' (Fig. 6). The quantity of $\tan\delta$ represents the ratio of dissipated energy to stored energy during one deformation cycle. Fig. 6a shows that for hydrogel without nanoparticles, $\tan\delta$ is around 0.03; i.e., G' is about 1.5 orders of magnitude higher than G'' so that its viscous properties are negligible. Addition of nanoparticles into these gels increases the viscous properties more strongly than the elastic properties, indicating that the dynamic adsorption/desorption equilibrium of the polymer chains with the particles dominates the elasticity of the gels [8]. Furthermore, it can be seen from Fig. 6b that with increasing cross-linker concentration, $\tan\delta$ decreases and approaches a limiting value of 0.04 at high concentration.

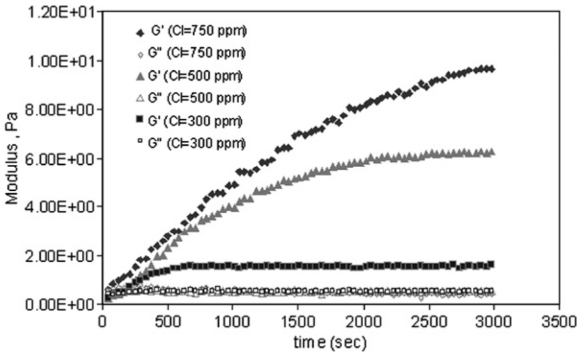

Fig. 5. Effect of cross-linker concentration on G' and G'' of the nanocomposite gels (polymer concentration: 5000 ppm, clay concentration: 500 ppm).

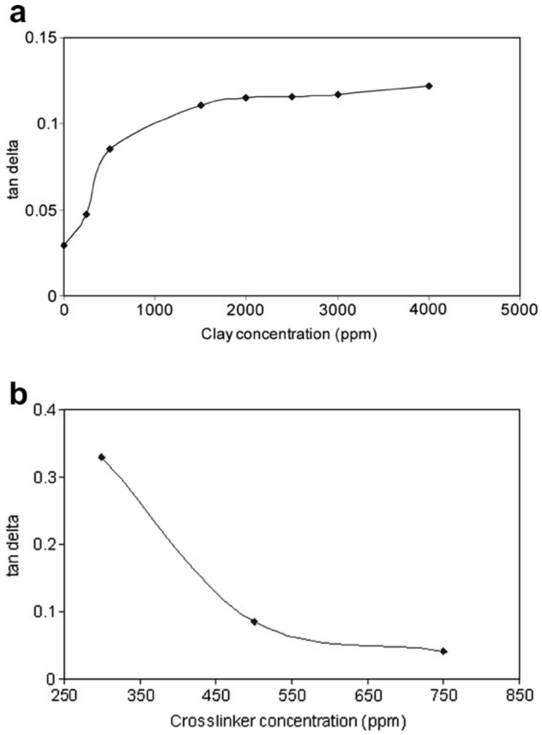

Fig. 6. Loss factor of the nanocomposite gels as a function of (a) nanoparticles concentration (polymer concentration: 5000 ppm, cross-linker concentration: 500 ppm) and (b) cross-linker concentration (polymer concentration: 5000 ppm, clay concentration: 500 ppm).

3.2. DLS and XRD analysis

In recent years dynamic light scattering method was successfully used for measuring the clay particle size in polymer-clay hybrids [36]. So we used this technique to determine the clay particle size in PAPMS solutions. The results were shown in Table 3. The Z-average particle sizes of the Na^+-MMT particles in PAMPS solution are between 169 nm and 728 nm. By comparing these values with particle length of the montmorillonite clays, which is about 100–200 nm [37], it seems that a few aggregates forms at high clay/polymer ratios.

The nature of the clay dispersion in wet NC hydrogels was elucidated by XRD measurements. Fig. 7 shows the

Table 3
Z-average particle sizes of Na^+-MMT in PAMPS solutions

Z-average particle size (nm)	Clay/polymer ratio (w/w)	Nanoclay concentration (ppm)
169	0.05	250
242	0.1	500
325	0.2	1000
456	0.4	2000
640	0.6	3000
728	0.8	4000

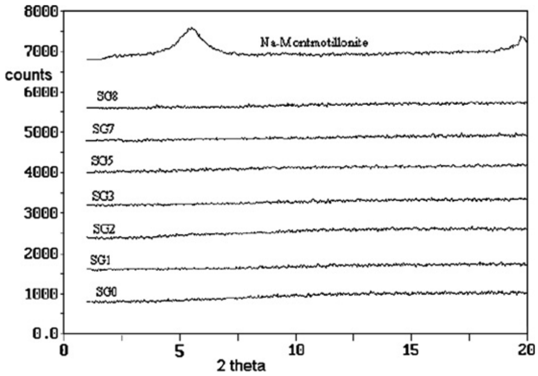

Fig. 7. XRD patterns of Na^+-MMT and conventional and PAMPS NC gels.

patterns of Na^+-MMT and conventional and nanocomposite sulfonated polyacrylamide hydrogels. Na^+-MMT shows an intensive peak at $2\theta = 5.8°$ which represents the diffraction form (001) crystal surface of silicate layers. The corresponding d-spacing in the silicate layers of Na^+-MMT is 1.522 nm. The patterns taken from the conventional and Na^+-MMT containing hydrogels do not show a characteristic basal reflection for all clay concentration; this might be interpreted to mean that the clay layers either are exfoliated or disordered. By considering the DLS results, the later is more probable.

3.3. Effect of clay on equilibrium swelling

The water absorbencies of the PAMPS/Na^+-MMT nanocomposite hydrogels in tap water are shown in Fig. 8. The results show that the equilibrium–swelling ratio of the PAMPS NC networks decreases with the increase of Na^+-MMT content. It was shown that the non-uniform distribution of the electric potential inside inhomogeneous polyelectrolyte gels leads to effective traps for the counterions [13]. The trapped counterions become osmotically passive and they do not contribute to the osmotic pressure, which is the main cause of gel swelling. In our case, inhomogeneity of charge and potential distribution comes from the anionic plates of the clay inside the gel. Most of the clay counterions remain mainly in the local volume around the clay particles or between the plates and do not contribute strongly to the total osmotic pressure inside the gel. Thus, counterions of Na^+-MMT, contrary to that of the sulfonated polyacrylamide chains, do not contribute significantly to gel swelling. Then the amount of hydrophilic groups in the NC network decrease with the increase of Na^+-MMT content, which causes the decrease of osmotic pressure difference between the polymeric network and the external solution, and then the shrinkage of the NC gel, occurs.

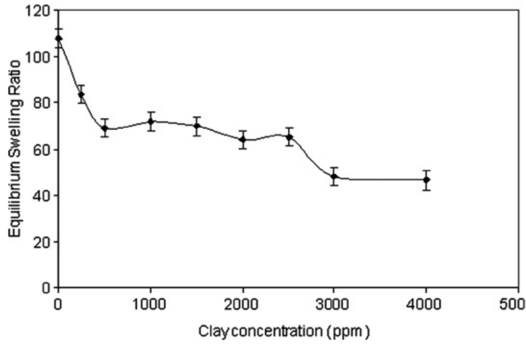

Fig. 8. Effect of Na^+-MMT content on equilibrium swelling ratio in tap water (polymer concentration: 5000 ppm, cross-linker concentration: 500 ppm).

3.4. Equilibrium swelling of NC hydrogels in electrolyte solutions

Considering the great impact of the external solutions on the swelling behavior of ionic gels and for expanding the applications of the NC polyacrylamide gels especially for enhanced oil recovery (EOR) purposes, the equilibrium swelling ratio of the prepared hydrogels were investigated in various electrolyte solutions. Figs. 9 and 10 show the effect of NaCl and $CaCl_2$ concentrations on ESR of NC hydrogels.

In addition, the effect of ionic strength of the external solution on the swelling was evaluated using the following relation [38]:

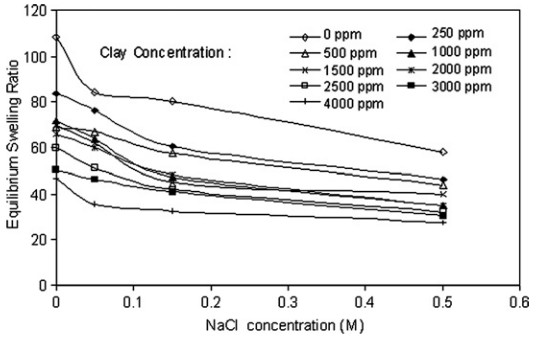

Fig. 9. Equilibrium swelling ratios of the NC hydrogels in NaCl Solution (polymer concentration: 5000 ppm, cross-linker concentration: 500 ppm).

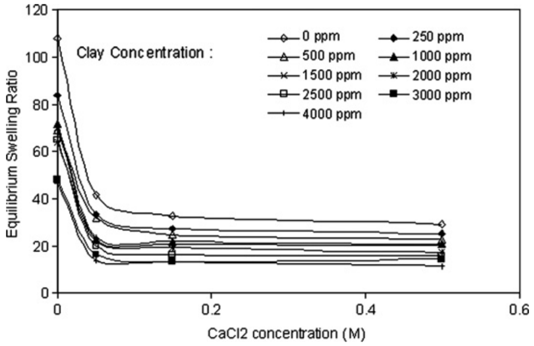

Fig. 10. Equilibrium swelling ratios of the NC hydrogels in $CaCl_2$ solution (polymer concentration: 5000 ppm, cross-linker concentration: 500 ppm).

$$Q_{eq}^{5/3} = A + Bi^2/I \quad (8)$$

Where Q_{eq} is the water absorbency at equilibrium (ESR), i is the concentration of the charges bound to the gel, I is the ionic strength of the external solution, and A and B are empirical parameters.

It can be seen from Figs. 9 and 10 and according to Eq. (8), the water absorbency of polyacrylamide NC hydrogels decrease with increasing of the ionic strength of the electrolyte solutions. This undesired phenomenon has been attributed to the reduction of the osmotic pressure difference between the polymeric network and the external electrolyte solution; according to Flory network theory [39]. Generally, the swelling ratio of polyelectrolyte gels depends on the association state of ionic groups within the polymer and on the affinity of the hydrogel for water [6]. The penetration of electrolyte solution counterions (Na^+ and Ca^{2+}) into the polymeric network makes the screening effect of them on the anionic groups ($-SO^{3-}$) of the polymer chain more evident, which leads to a non-perfect anion–anion electrostatic repulsion and consequently to the water absorbency reduction. It also can be seen from Figs. 9 and 10 that for a given concentration of salt solution, the water absorbency in NaCl solution is higher than that in $CaCl_2$ solution. This result is due to the complexing ability of the anionic sites of chains and divalent cation (Ca^{2+}), leading to a decreased osmotic pressure of the ionic network and an increased degree of ionic cross-linking which results in loss of swelling [40].

Due to the applications of the polyacrylamide gels in enhanced oil recovery treatments for control of the excess water production, swelling behavior of the prepared NC gels were investigated in the synthetic oil reservoir water. Fig. 11 compares the swelling behaviors of NC gels in tap and synthetic oil reservoir water. As can be seen from this figure, the NC gels have lower swelling capacity in oil reservoir water due to presence of mono-and multivalent cations in the oil reservoir water (Table 2). In addition the ESR of NC gels in oil reservoir water decreases with the increasing of Na^+-MMT content. The explanations of these results are similar to those of the previous sections.

Fig. 12 shows the salt sensitivity of the NC gels containing different clay concentration. The NC gels have lower salt sensitivity factor in synthetic oil reservoir water, compared with unfilled gel; that is, the deswelling of the swollen sample was more evident for conventional PAMPS network. This can be attributed to the higher mobility of the PAMPS chains in the conventional gel, which allow it to exhibit higher deswelling behavior. These results suggest the superior swelling behavior of the PAMPS/chromium acetate/clay hydrogels in oil reservoir water.

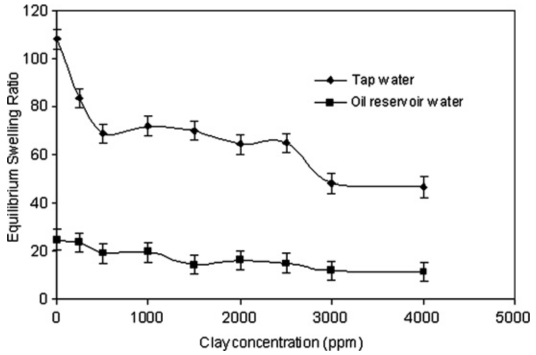

Fig. 11. Swelling behaviors of the NC gels in tap and synthetic oil reservoir water (polymer concentration: 5000 ppm, cross-linker concentration: 500 ppm).

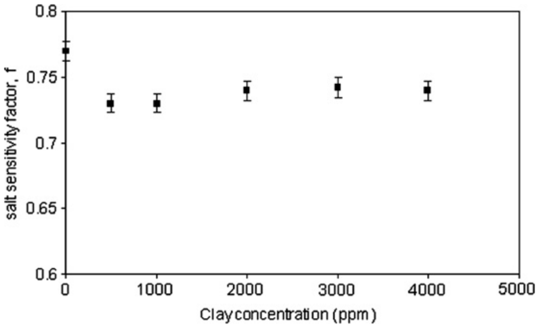

Fig. 12. Salt sensitivity of the NC gels with different clay content (polymer concentration: 5000 ppm, cross-linker concentration: 500 ppm).

The PAMPS/Cr^{3+} gelling systems are commercial gels in enhanced oil recovery applications [41,42]. We compared the viscoelastic properties and ion resistance of the PAMPS/Cr^{3+}/clay nanocomposite hydrogels with unfilled PAMPS/Cr^{3+} hydrogels in Figs. 4 and 12, respectively. One can see that our PAMPS/Cr^{3+}/clay nanocomposite hydrogels have higher storage modulus and ion resistance than unfilled PAMPS/Cr^{3+} hydrogels; as a consequence they are potentially good candidates for application in enhanced oil recovery.

4. Conclusions

The gelation behavior and the effect of the clay content and electrolyte type and concentration on the swelling behavior of the PAMPS nanocomposite hydrogels, prepared by cross-linking of partially hydrolyzed polyacrylamide/sodium montmorillonite aqueous solutions with chromium triacetate, were investigated. Study of the gelation behavior showed that the limiting storage modulus of the NC gels decreased with increasing clay content up to 1000 ppm, but it decreased by further increase of Na^+-MMT loading in the NC gels. It was also found that with increasing the clay content, the viscous energy dissipation properties of the nanocomposite gels increased. With increasing cross-linker concentration, the gelation point appears sooner; indicating that Cr^{3+} cross-linking of polyacrylamide is the rate-limiting reaction. Studies of swelling behavior showed that the equilibrium swelling ratio of the PAMPS nanocomposite networks decreases with the increase of Na^+-MMT content. In addition, the water absorbency of sulfonated polyacrylamide NC hydrogels decreased with increasing the ionic strength of the swelling media. However, nanocomposite gels showed lower salt sensitivity in electrolyte solutions as compared with unfilled gels. The swelling behavior and rheological properties of these nanocomposite hydrogels make them potentially good candidates for enhanced oil recovery applications.

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