FULL LENGTH ARTICLE

Solution properties of hydrophobically modified polyacrylamides and their potential use for polymer flooding application

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Abstract We tested nine hydrophobically modified polyacrylamides with molecular weights situated between 1.58 and 0.89×10^6 g/mol for enhanced oil recovery applications. Their solution properties were investigated in the distilled water, brine solution, formation water and sea water. Their critical association concentrations were determined from the relationship between their concentrations and the corresponding apparent viscosities (η_{app}) at 30 °C at shear rate 6 s^{-1}. They were between 0.4 and 0.5 g/dl. The brine solutions of 0.5 g/dl of HM-PAMs were investigated at different conditions regarding their apparent viscosities. Such conditions were mono and divalent cations, temperature ranging from 30 to 90 °C, the shear rate ranging from 6 to 30 s^{-1} and the aging time for 45 days. The surface and interfacial tensions for the HM-PAMs were measured for concentration range from 0.01 to 1 g/dl brine solutions at 30 °C and their emulsification efficiencies were investigated for 7 days. The discrepancy in the properties and efficiencies of the tested copolymers was discussed in the light of their chemical structure.

1. Introduction

After conventional water-flooding processes (secondary recovery), the residual oil in the reservoir remains as a discontinuous phase in the form of oil drops trapped by capillary forces and is likely to be around 70% of the original oil left in place.

Chemical flooding has proved to be an effective method to enhance the oil recovery. Polyacrylamide (PAM) is one of the most widely used polymers in the chemical flooding (polymer flooding). However, there are many defects in its practical application, such as low temperature resistance, poor salt tolerance, and easy oxidative degradation. Also, PAM cannot emulsify the oil–water system, which limits its oil recovery capability. In order to reduce the oil–water interfacial tension and enhance the emulsification process to improve the displacement efficiency, the binary flooding systems of PAM-

Table 1 Abbreviations, intrinsic viscosities [η] and molecular weights of the HM PAMs and PAM.

Group	Abbreviation	[η] (ml/g)	Molecular weight [g/mol]	
			$M\eta \times 10^6$	$Mw \times 10^6$
Group I	PAM-Ia (Poly(AM-co-OSA-eo22Ac))	316	1.09	1.29
	PAM-Ib (Poly(AM-co-DDSA-eo22Ac))	320	1.11	1.58
	PAM-Ic (Poly(AM-co-ODSA-eo22Ac))	336	1.18	1.09
Group II	PAM-IIa (Poly(AM-co-O-DDS-eo22Ac))	312	1.07	1.07
	PAM-IIb (Poly(AM-co-TD-DDS-eo22Ac))	286	0.95	0.93
	PAM-IIc (Poly(AM-co-OD-DDS-eo22Ac))	282	0.93	0.98
Group III	PAM-IIIa (Poly(AM-co-O-OS-eo22Ac))	288	0.96	0.95
	PAM-IIIb (Poly(AM-co-DD-DDS-eo22Ac))	296	1.01	1.22
	PAM-IIIc (Poly(AM-co-OD-ODS-eo22Ac))	293	0.99	0.89
–	PAM (Polyacrylamide)	757	3.5	3.44

surfactant or PAM-surfactant-alkali tertiary combination were developed [1–3]. However, for these combined systems, the use of a large amount of surfactant leads to a high cost, and the presence of alkali causes problems such as the separation of oil from water and waste water treatment [4]. To overcome these difficulties, the modified polymer systems such as hydrophobically modified polyacrylamides that can enhance the viscosity, increase the interface activity, and improve the emulsification ability without the addition of surfactant and alkali were suggested [5].

Hydrophobically modified polymers are water-soluble polymers that contain a small amount of hydrophobic groups directly linked to the main chain of the polymer. In aqueous solutions, the hydrophobic groups of these polymers tend to associate to minimize their exposure to the aqueous medium, analogous in a way to the micelle formation of a surface agent above its critical micellar concentration. Such associations result in an increase of the hydrodynamic size, which increases solution viscosity. Because the high viscosity conveyed by these polymers is attributed to molecular association, on shearing the fluids just disrupt these associations, which are reset when shear is interrupted and initial viscosity is recovered [6–12].

Furthermore, in view of the amphiphilic structure (i.e. the presence of hydrophobic moieties in the mainly hydrophilic polymer chain) of most hydrophobically associating polymers, these polymers can also exhibit simultaneously high surface and interfacial activities. The amphiphilic polymers form monomolecular or polymolecular micelles in aqueous solutions [13–15], and thus have enhanced ability to adsorb on the interface. This can lead to a sharp reduction in the surface and interfacial tensions (IFTs) of the polymer solution. The combination of rheological behavior (i.e. thickening properties), surface and interfacial activities of these polymers can be of great technological interest, especially in a number of important commercial applications such as enhanced oil recovery (EOR), drag reduction, flocculation, super absorbency, latex paints, hydraulic fluids, protein separations, industrial thickeners, controlled drug release and biological/medical purposes [16].

In this paper, our object is to investigate the solution properties and the rheological properties of high molecular weight hydrophobically modified polyacrylamides prepared as previously described [17] with respect to their concentration, shear rate, temperature, aging and different cations' concentration. Our attention should be extended to investigate the surface

and IFT behavior of these copolymers in the presence of NaCl in terms of variation of concentration.

2. Experimental

2.1. Materials

Sodium chloride and calcium chloride were used in analytical grade. The aqueous solutions were prepared using double distilled water, brine solution (0.1 mol/l NaCl), formation water (received from Khalda Petroleum Company), sea water (from the red sea) and the crude oil (received from Bader El-Din Petroleum Company). The hydrophobically modified polyacrylamides were synthesized in the previous work [17]. The prepared copolymers were divided into three groups I, II and III. Their abbreviations and molecular weights are listed in Table 1.

2.2. Measurements and analysis

2.2.1. Surface and interfacial tensions
Different concentrations from 0.01 to 1 g/dl of the prepared HM-PAMs were dissolved in the brine solution and their surface and interfacial tensions with a mixture of n-hexane and cyclohexane were measured at 30 °C using Lecomte De Nouy tensiometer ring (Kruss Gmbh, Hamburg, Germany). The instrument was daily regulated by double distilled water [18].

2.2.2. Rheological measurements
The solutions of polymer (PAM) and copolymers (HM-PAMs) for rheological measurements were prepared by dissolution of accurately weighed quantities of polymer and copolymers in the double-distilled water, brine solution, formation water and sea water at room temperature. The polymers were allowed to hydrate and swell for 1–3 days; then the solutions were very gently stirred magnetically for 7–10 days to form homogeneous solutions. The prepared solutions were heated on a water bath at 50 °C for 24 h to remove the air bubbles. The samples were carried out using a Brookfield LVDV-III Ultra Programmable Rheometer with Cone/Plate Viscometers (Brookfield Engineering Laboratories, Inc., Middleboro, MA 02346-1031, USA) using cone spindle (CPE-40), which had a full scale range of (0.15 – 3065 cP) with an accuracy of ±1% of full scale range viscometer. The apparent viscosities

(η_{app}) of each aqueous solution as a function of the polymer and copolymer concentration were recorded at 30 °C at shear rate 6 s^{-1}, while those recorded as a function of electrolyte concentration (mono and divalent), temperature, shear rate and aging were measured for 0.5 g/dl brine solutions of the polymer and copolymers.

2.2.3. Emulsification

The emulsion samples were prepared by mixing the crude oil and the polymer or copolymer brine solutions (O/W ratio 1/1 (v/v)) in a 160 ml scaled glass. The emulsification was carried out by shaking for 200 times. The stability of the emulsion was observed at 30 ± 0.1 °C for a period of 7 days [5].

3. Results and discussion

3.1. Solution properties of PAM and HM-PAMs

3.1.1. Critical association concentration (C^*) and effect of concentration on apparent viscosity (η_{app})

The dependence of the apparent viscosities (η_{app}) of the hydrophobically modified polyacrylamides (HM-PAMs) on their concentrations was estimated in different aqueous solutions such as; distilled water, brine solution (0.1 mol/l NaCl), formation water and sea water which are shown in Figs. 1–3.

For all the relationship curves, the apparent viscosities η_{app} increased by increasing the polymer and copolymer concentration. At a certain concentration, an obvious increase in the η_{app} values appeared and above this concentration the apparent viscosities enhanced remarkably with increasing concentrations of the copolymers. The fact indicates that, this concentration is the transforming concentration from the intramolecular hydrophobic association to the intermolecular hydrophobic association, i.e. it is the critical association con-

centration (CAC), denoted as C^*. Over the value of C^* the distance between the macromolecules decreased and the extent of the intermolecular associations was strengthened, resulting in the augment of the association network volume and the increase of the association network number. This caused also an increase of the apparent viscosities by a large margin. By plotting the two tangents of these curves about the point at which an obvious increase of apparent viscosity appeared, the critical association concentrations C^* can be determined. The C^* values are corresponding to the concentrations of the intersection points for the two tangents. For all the nine copolymers in the different aqueous solutions, the critical association concentrations (C^*) situated between 0.4 and 0.5 g/dl [19].

For the copolymers of group I, Fig. 1(a–d) shows the relationship curves in the different media. For each aqueous solution, the values of η_{app} increased by increasing the hydrophobic chain length, where, the longer side chain caused a stronger association which prevented the curliness of the copolymer [20,21]. As the hydrophobic side chain length increased as; C$_8$, C$_{12}$ and C$_{18}$ for PAM-Ia, PAM-Ib and PAM-Ic respectively, the corresponding η_{app} values increased in that order. The η_{app} values for PAM-Ia in each aqueous solution were lower than the η_{app} values for the PAM-Ib, and they further were lower than the values of PAM-Ic.

The values of η_{app} in distilled water of group I were higher than its values in brine solution and formation water, but the η_{app} values were small in sea water. This diversity in the values of η_{app} for the solutions of group I copolymers in different media may be due to the far location of the ionic group in the surfmer portion from the copolymer backbone and near from the hydrophobic side chain which affected their η_{app} values. The decreasing values of η_{app} were expected as a result of shielding the ionic charges on the copolymer chains in the presence of mono or divalent cations in the aqueous solutions.
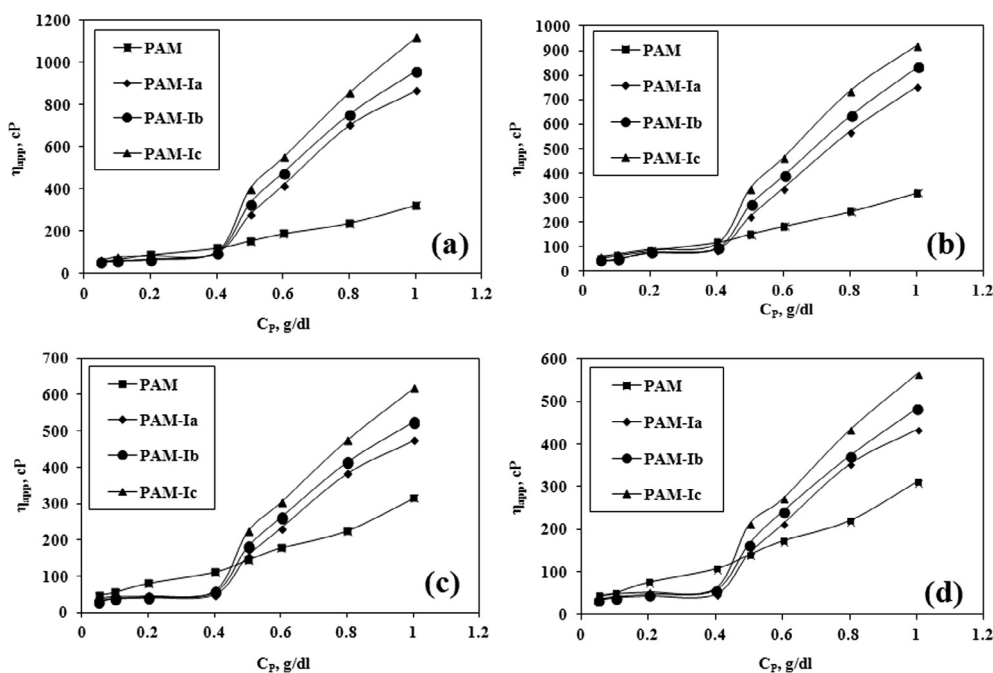

Figure 1 Dependence of apparent viscosity on the concentration of PAM, PAM-Ia, PAM-Ib and PAM-Ic in (a) distilled water (b) brine solution (c) formation water and (d) sea water at 30 °C and 6 s^{-1}.

Figure 2 Dependence of apparent viscosity on the concentration of PAM-IIa, PAM-IIb and PAM-IIc in (a) distilled water (b) brine solution (c) formation water and (d) sea water at 30 °C and 6 s^{-1}.
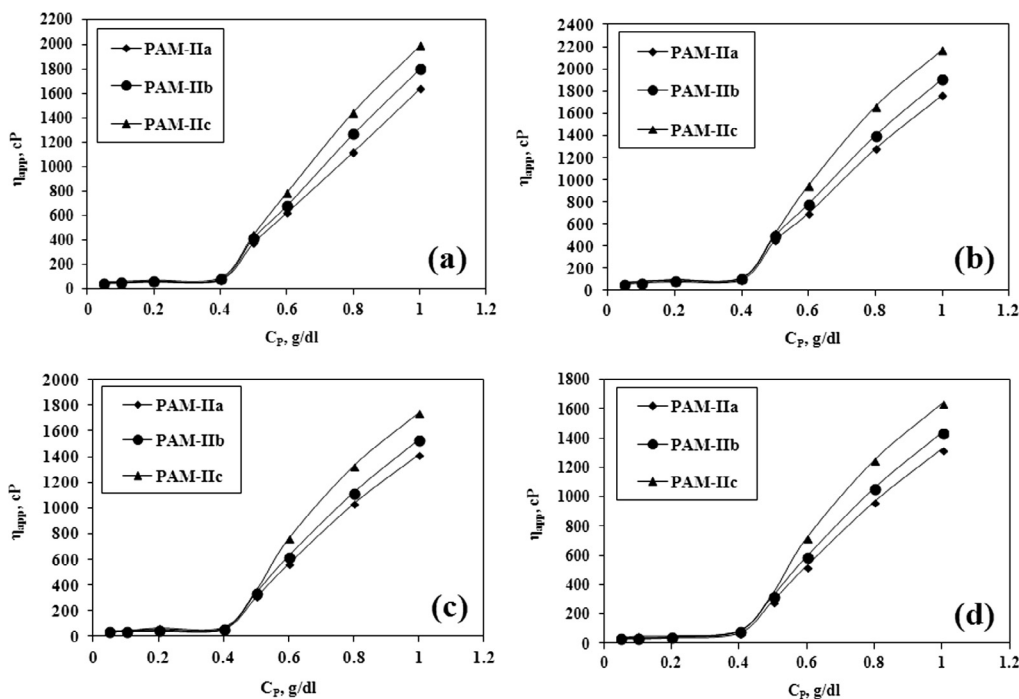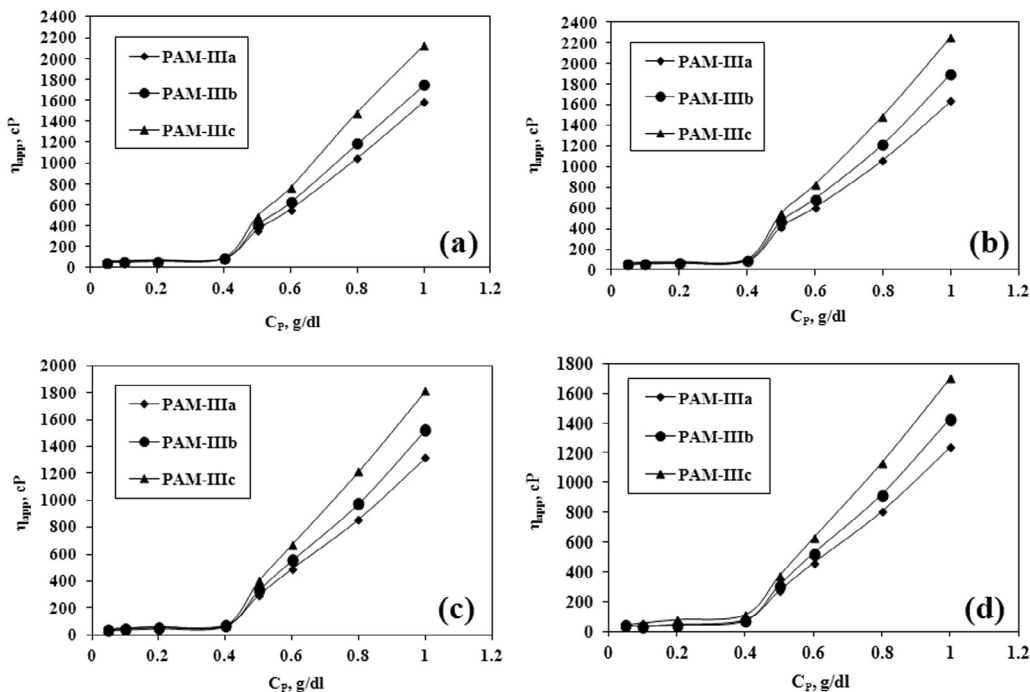

Figure 3 Dependence of apparent viscosity on the concentration of PAM-IIIa, PAM-IIIb and PAM-IIIc in (a) distilled water (b) brine solution (c) formation water and (d) sea water at 30 °C and 6 s^{-1}.

These ionic charges act as an electrostatic shield between the –COOH anions which are suspended on the surfmer part. The shielding effect reduces the carboxylate repulsion of the copolymer backbone, leading to reduce the molecular coil size which reflected on decreasing the η_{app} values [22,23]. For example, the η_{app} values at concentration 0.5 g/dl for the PAM-Ia, PAM-Ib and PAM-Ic in the distilled water were 279, 333 and 404 cP respectively, but in the brine solution they were 222, 272 and 338 cP, while they were 155, 181 and 222 cP in the formation water and finally 144, 166 and 212 cP in the

sea water. In high salinity solutions, the reduction magnitude of the η_{app} values in both the formation water and the sea water due to the presence of mono and/or divalent ions was about 45–50% of their initial η_{app} values in the distilled water. This reduction magnitude suggested that these copolymers have slightly good salt-resistant properties in spite of the presence of ionic groups in their chemical structure and may be used in the enhanced oil recovery applications.

The dependence of η_{app} values of group II HM-PAMs on their concentration in different aqueous media is shown in Fig. 2(a–d). In the chemical structure of the copolymers, the surfmers incorporated in the backbones are double tailed surfmers with the second tail length increased from C_8 to C_{14} and C_{18} by esterification with different alcohols for PAM-IIa, PAM-IIb and PAM-IIc respectively. So that, they show the same performance as copolymers of group I, where the values of η_{app} increased with increasing the length of the second hydrophobic side chain in each aqueous solution. For example, the η_{app} values of 0.5 g/dl obtained for PAM-IIa were 297, 393, 233 and 212 cP (in the distilled water, brine solution, formation water and sea water respectively), while those obtained for PAM-IIb were 333, 444, 272 and 255 cP, but the values of η_{app} for PAM-IIc were 393, 494, 309 and 299 cP. Also, it was clear that the values of η_{app} which were obtained for the three copolymers of group II in the brine solution were higher than the values obtained in the distilled water. For 0.5 g/dl of PAM-IIa, PAM-IIb and PAM-IIc the values of η_{app} in the distilled water were 297, 333 and 393 cP but in the brine solution were 394, 444 and 494 cP. This maybe attributed to the presence of 0.1 mol/l NaCl which makes the aqueous environment more hostile for the hydrophobic chains causing them to favor association with each other, and hence promoting the formation of large macromolecular aggregates [24]. Salt reduces the quality of the solvent because many of the water molecules are consumed during dissolving the salt ions and consequently, less water molecules are available for dissolving the copolymer molecules. This forces the copolymer molecules to favor interacting with each other over interacting with the solvent molecules, and consequently they tend to form intermolecular aggregates through the hydrophobic chains [16]. Since the values of η_{app} in the brine solution enhanced with a certain degree, it can be concluded that, these copolymers have positive sensitivity and sensibility toward a certain range of NaCl concentrations. The η_{app} values obtained for PAM-IIa, PAM-IIb and PAM-IIc in the formation and sea water were lower than the initial values obtained in the distilled water. The magnitude of reduction for the values of η_{app} did not exceed more than 20–25% for formation and sea water respectively. This reduction in the η_{app} values may be due to the presence of mono and divalent ions in formation and sea water which favored or enhanced intramolecular association interactions and the hydrophobic microstructures to become more compact. Also it was noticed that, when the salt concentration increases the condensed aggregates associate to form larger aggregates and the values of η_{app} decreased [23,25]. This magnitude of reduction suggested that these copolymers have good salt-resistant properties and can be used in the enhanced oil recovery applications.

The relationship curves in the different aqueous media for the copolymers of group III are shown in Fig. 3(a–d). The surfmers incorporated in the backbones are double twin tailed surfmers with the length of each tail increased from C_8 for

PAM-IIIa to C_{12} for PAM-IIIb then C_{18} for PAM-IIIc. The obtained values of the η_{app} for the three copolymers of group III in different aqueous solutions were similar as shown for the copolymers of group II. For each aqueous media, the η_{app} values increased by increasing the hydrophobic side chain length, the values for PAM-IIIa were lower than those for PAM-IIIb which in turn are lower than the values for PAM-IIIc. Also, the values of η_{app} for the three copolymers in brine solution were higher than the values in distilled water and those obtained in both formation and sea water were lower than the initial values obtained in distilled water. The magnitude of reduction of η_{app} values was about 20–25% for formation and sea water respectively.

This reduction in η_{app} values maybe due to the presence of mono and divalent ions in formation and sea water [23,25]. The values of η_{app} corresponding to 0.5 g/dl for PAM-IIIa, PAM-IIIb and PAM-IIIc in the distilled water were 218, 303 and 398 cP, in the brine solution were 287, 340 and 460 cP, in the formation water were 177, 242 and 313 cP and finally in the sea water were 161, 222 and 303 cP. All the above results suggested that these copolymers are similar in their solution behavior such the copolymers of group II. They all have positive salt sensitivity and salinity sensibility at a certain range of NaCl concentrations, and they have also good salt-resistant properties in another certain range of cations (for mono and divalent ions).

The unmodified polyacrylamide homopolymer (PAM) was compared to the above copolymers of the three groups. No such critical association concentration (C^*) was observed through the investigation of concentration range for each PAM aqueous solution (distilled water, brine solution, formation water and sea water). The values of η_{app} increased gradually with increasing concentrations and slightly differ from solution to another. It has a good salt resistance. The η_{app} values for 0.5 g/dl PAM and higher concentrations in different aqueous media were all lower than those for the nine HM-PAMs.

3.1.2. Effect of sodium chloride (monovalent cations)

The dependence of the apparent viscosities (η_{app}) of 0.5 g/dl in brine solutions for the HM-PAMs of the three groups (I, II and III) on sodium chloride concentration at 30 °C and shear rate 6 s^{-1} is illustrated in Fig. 4(a–c). For the copolymers of group I, the values of η_{app} decreased rapidly from 222, 292 and 363 cP to 77, 95 and 108 cP for PAM-Ia, PAM-Ib and PAM-Ic respectively by increasing the NaCl concentration from 0 to 0.4 mol/l. This can be attributed to the ionic shielding on the carboxylate groups (–COOH) which is present in the chemical structure of the surfmers incorporated in the copolymers of group I [22]. The shielding effect reduces the carboxylate repulsion of the copolymer backbone, leading to a reduction in the molecular coil size and the weakened intermolecular associations, further the decrease in their apparent viscosities was obtained [23]. However, in the range of 0.4–0.7 mol/l NaCl, the η_{app} values increased gradually from 77, 95 and 108 cP to 117, 149 and 184 cP for the PAM-Ia, PAM-Ib and PAM-Ic respectively, this may be due to the charge shielding effect tended to reach the equilibrium, and the solution polarity induced by increasing of the electrolyte in terms of NaCl concentration. Also, the complexation of the C–O bonds in the ethylene oxide side chains in the chemi-
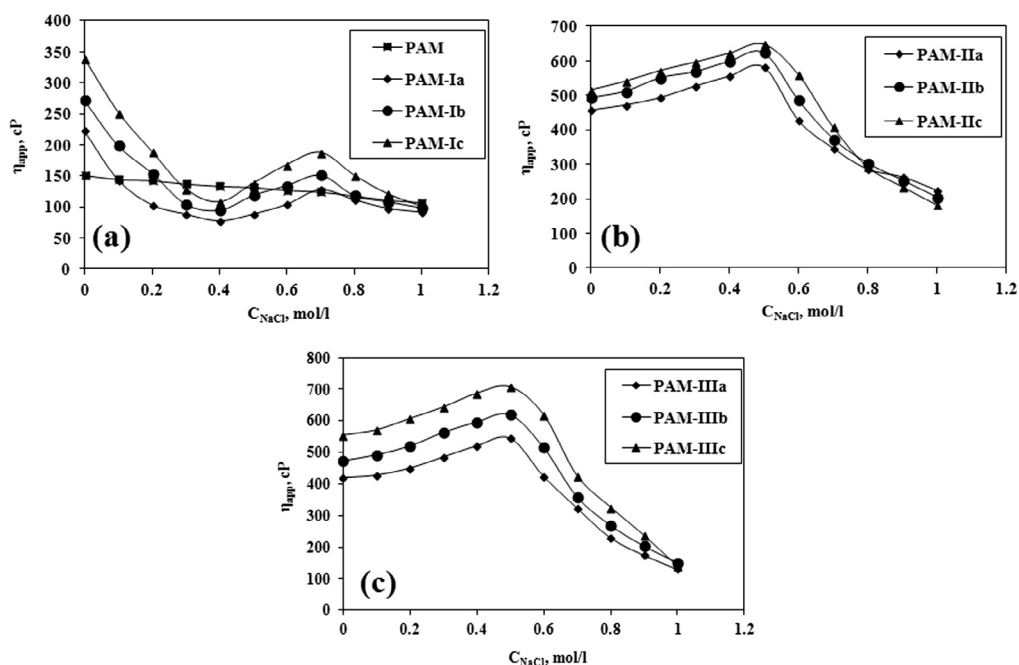
Figure 4 Effects of NaCl Concentration on Apparent Viscosity of (a) PAM and Group I, (b) Group II and (c) Group III Brine Solutions at 30 °C and 6 s^{-1}.

cal structure of the surfmers with Na$^+$ ions, which decreased the hydrophilicity of EO chains enhanced the intermolecular associations of the alkyl groups. This finally leads to reinforce the intermolecular hydrophobic associations and a salt-thickening effect appeared [26]. In the range of 0.7–1 mol/l of NaCl, the hydrophobic microstructures became more compact because the intermolecular hydrophobic associations were being stronger and the hydrodynamic volumes decreased. Hence, the η_{app} values reduced from 117, 149 and 184 cP to 91, 99 and 101 cP.

For the copolymer of group II and III, the values of η_{app} increased gradually by increasing the NaCl concentration from 0 to 0.5 mol/l. This was attributed to an increase in the solution polarity which was induced by electrolytes. This polarity leads to reinforce the intermolecular hydrophobic associations and a good salt-thickening behavior appeared [25]. They increased from 393, 444 and 494 cP to 514, 560 and 616 cP for the PAM-IIa, PAM-IIb and PAM-IIc respectively and from 288, 404 and 531 cP to 444, 584 and 716 cP for the PAM-IIIa, PAM-IIIb and PAM-IIIc.

However, in the range from 0.5 to 1 mol/l NaCl, the η_{app} values decreased from 514, 560 and 616 cP to 224, 205 and 183 cP for the PAM-IIa, PAM-IIb and PAM-IIc respectively and from 444, 584 and 716 cP to 132, 152 and 140 cP for the PAM-IIIa, PAM-IIIb and PAM-IIIc. This is because the hydrophobic microstructures became more compact, and then the condensed aggregates associated to form larger aggregates, resulted in the phase separation of gels and the apparent viscosities decreased [22,24].

For comparison, the effect of sodium chloride concentration on the values of η_{app} of 0.5 g/dl PAM in the brine solution and shear rate 6 s^{-1} at 30 °C is shown in Fig. 4a. It is clear that, the values gradually decreased with increasing NaCl concentration and the η_{app} value decreased from 150 to 107 cP.

3.1.3. Effect of calcium chloride (divalent cations)

The apparent viscosities (η_{app}) in the brine solutions for the HM-PAMs of the three groups as a function of calcium chloride concentration at 30 °C, shear rate 6 s^{-1} and 0.5 g/dl are shown in Fig. 5(a–c).

The values of η_{app} for the copolymers of group I decreased rapidly from 222, 292 and 363 cP to 96, 137 and 176 cP in the range of 0–0.04 mol/l CaCl$_2$ for the PAM-Ia, PAM-Ib and PAM-Ic respectively, and then they tended to increase slightly to 113, 148 and 183 cP at 0.05 mol/l CaCl$_2$. This may be due to the reinforcement of the intermolecular associations of the hydrophobic groups. Above 0.05 mol/l CaCl$_2$, the values of η_{app} decreased gradually from 113, 148 and 183 cP to 47, 50 and 47 cP.

For the copolymers of group II and III, the effect of CaCl$_2$ on the values of η_{app} was similar, the η_{app} values increased slightly from 393, 444 and 484 cP to 424, 479 and 521 cP for the PAM-IIa, PAM-IIb and PAM-IIc and from 288, 404 and 531 cP to 384, 498 and 607 cP for the PAM-IIIa, PAM-IIIb and PAM-IIIc at concentration range from 0 to 0.02 mol/l CaCl$_2$. Then they decreased in the range between 0.02 and 0.1 mol/l CaCl$_2$ to the values 116, 104 and 91 cP for the PAM-IIa, PAM-IIb and PAM-IIc and 96, 75 and 62 cP for the PAM-IIIa, PAM-IIIb and PAM-IIIc. The electrostatic shielding effect of the divalent Ca^{+2} ion on repulsive interaction was stronger than that of Na$^+$ ion [26]. The maximum CaCl$_2$ concentration is usually lower than 5 g/l for the oil reservoirs with a high salinity. Hence, the HM-PAMs of group I exhibited a slightly divalent cation resistance while those of group II and III exhibited a good resistance.

The effect of calcium chloride concentration on the apparent viscosity η_{app} of 0.5 g/dl PAM in the brine solution was investigated and illustrated in Fig. 5a. In a concentration range 0.01–0.1 mol/l CaCl$_2$, the value of η_{app} decreased gradually
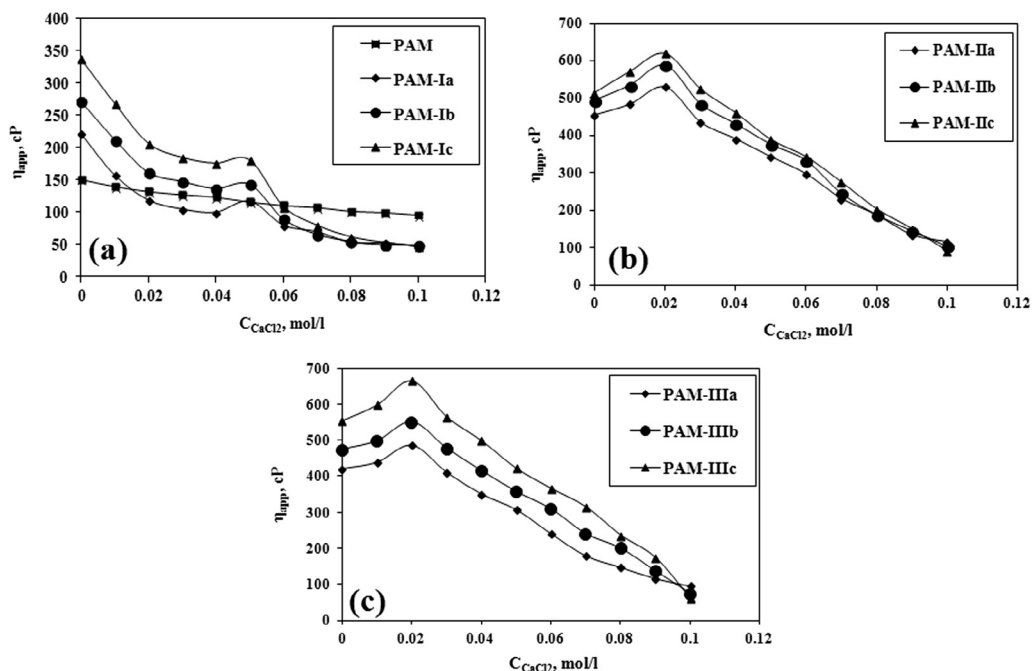
Figure 5 Effects of $CaCl_2$ concentration on apparent viscosity of (a) PAM and group I, (b) group II and (c) group III brine solutions at 30 °C and 6 s^{-1}.

from 151 to 95 cP. It has been reduced by a magnitude about 37%, which shows that the divalent Ca^{+2} ion is stronger than the monovalent Na^+ ion.

3.1.4. Effect of temperature

The effect of temperature on the apparent viscosities (η_{app}) for 0.5 g/dl of the tested HM-PAMs of the three groups (I, II and

III) in the brine solution at shear rate 6 s^{-1} is shown in Fig. 6 (a–c).

As can be expected, a decrease in the η_{app} values was observed for all the copolymers with increasing temperature. The lowering of the solution viscosity with increasing temperature has been reported before for aqueous solutions of hydrophobically associating water-soluble polymers [16]. This
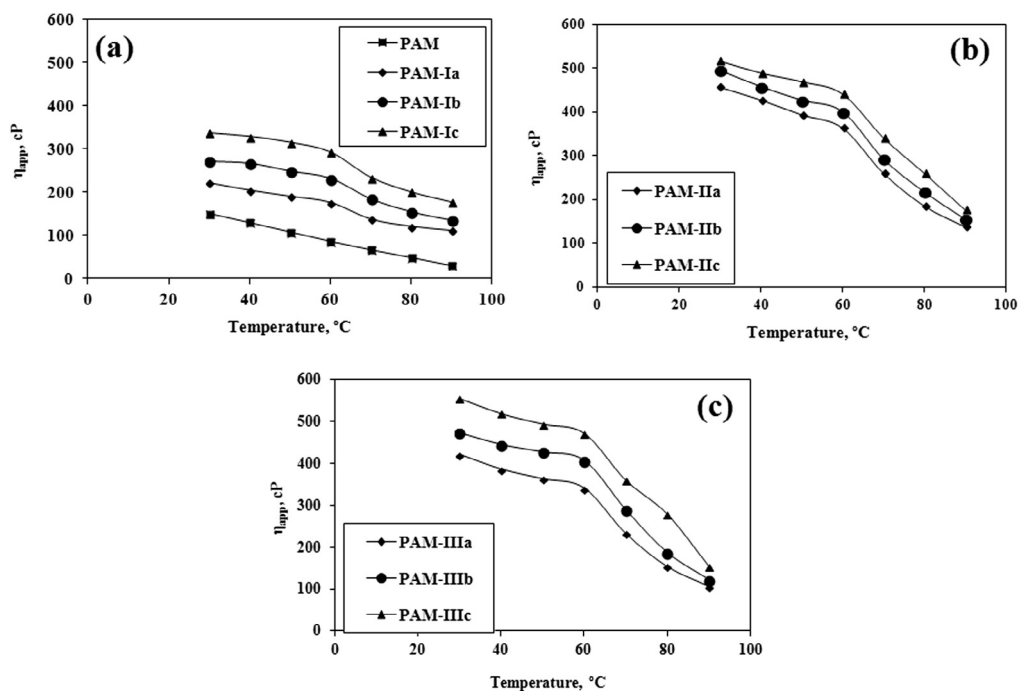

Figure 6 Effect of temperature on apparent viscosity of (a) PAM and group I, (b) group II and (c) group III brine solutions at 6 s^{-1}.
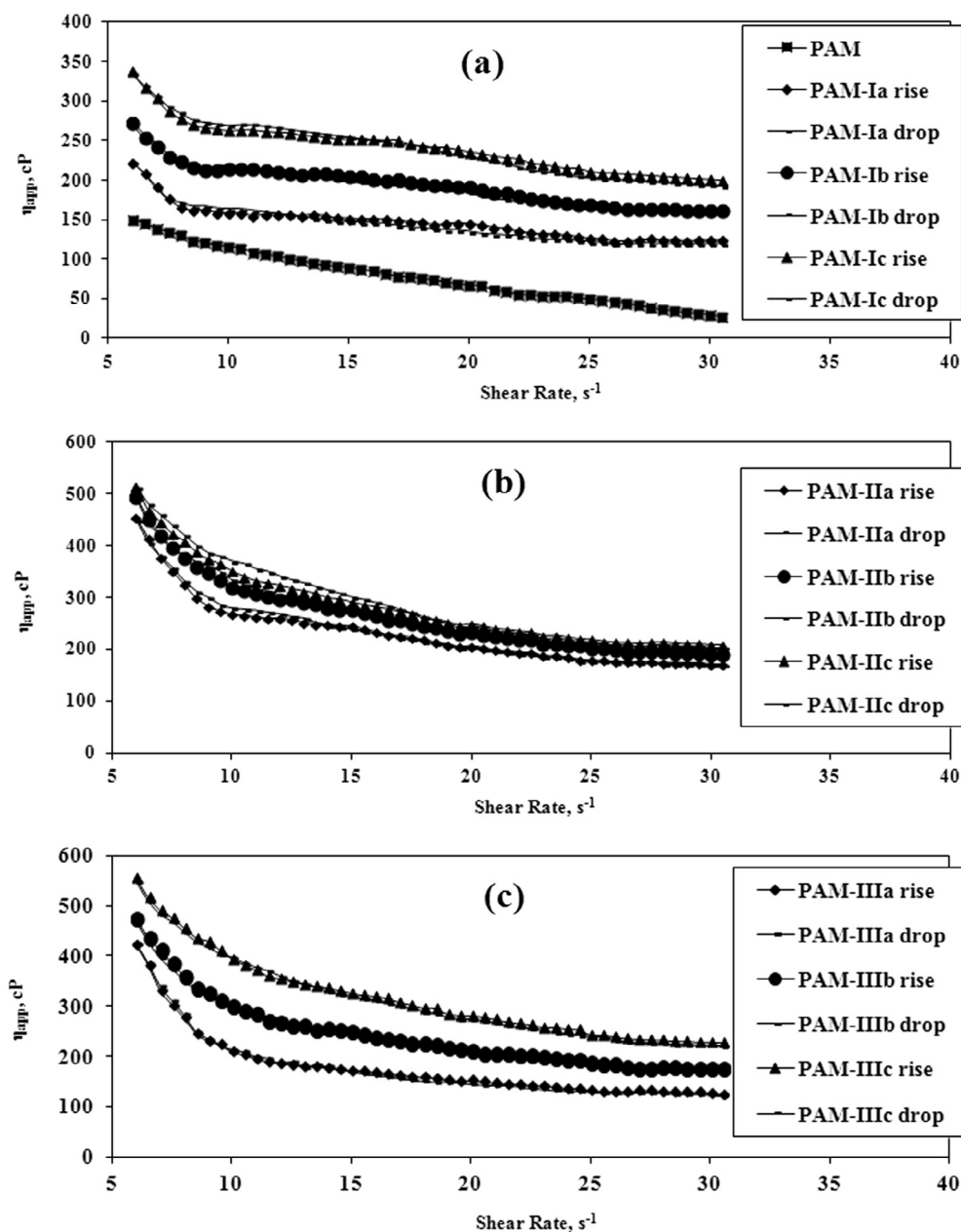
Figure 7 Effect of shear rate on apparent viscosity of (a) PAM and group I, (b) group II and (c) group III brine solutions at 30 °C.

effect could be attributed to the weakening of the hydrophobic effect at elevated temperatures due to increase the mobility of the copolymer chains (as a result of decrease in the solvent viscosity). This finding gives rise to loss of inter-chain liaisons and/or an increase in the solubility of the copolymers as temperature increases.

For the copolymers of group I, the decline of η_{app} values takes three stages. The first stage was from 30 to 60 °C, the η_{app} values smoothly decreased from 222, 292 and 365 cP to 176, 232 and 293 cP for the PAM-Ia, PAM-Ib and PAM-Ic respectively. The second stage was from 60 to 70 °C, where the η_{app} values decreased sharply to 138, 185 and 235 cP. Finally, from 70 to 90 °C, the η_{app} values decreased gradually from 138, 185 and 235 cP to 108, 136 and 178 cP for the PAM-Ia, PAM-Ib and PAM-Ic respectively.

For the copolymers of group II and III, the decline of the η_{app} values passes through two stages only. The first stage was in the temperature range from 30 to 60 °C, where the decrease of the η_{app} values was gradual. But in the second stage, the decrease was sharply in the range of 60–90 °C. For the PAM-IIa, PAM-IIb and PAM-IIc the values of η_{app} at 60 °C were 277, 322 and 386 cP respectively and decreased to 129, 155 and 176 cP at 90 °C. But for the PAM-IIIa, PAM-IIIb and PAM-IIIc, the values of η_{app} at 60 °C were 223, 317 and 426 cP respectively and decreased to 102, 132 and 173 cP at 90 °C.

The above three groups of copolymers exhibited various temperature resistance. The values of η_{app} for the copolymers of group I maintained about 50% of their initial values at elevated temperature (90 °C), so they showed good temperature

Table 2 Effect of aging on the apparent viscosities of PAM and HM-PAMs at 55 °C from 1 to 45 days.

Sample	Aging time/day						
	0	1	5	10	15	30	45
PAM	152	151	144	140	138	131	114
PAM-Ia	222	220	212	202	192	185	177
PAM-Ib	292	290	280	265	252	241	232
PAM-Ic	363	361	349	331	320	311	292
PAM-IIa	393	396	391	383	376	357	336
PAM-IIb	444	442	435	426	414	397	379
PAM-IIc	494	494	490	482	471	451	422
PAM-IIIa	288	284	277	270	262	257	246
PAM-IIIb	404	400	393	376	363	350	343
PAM-IIIc	530	531	511	499	477	464	454

resistance. The values of η_{app} for the copolymers of group II and III lose about 60% and 70% of their initial values at elevated temperature (90 °C) respectively, so they showed slight temperature resistance.

The effect of temperature on the apparent viscosity η_{app} of 0.5 g/dl PAM in the brine solution is illustrated in Fig. 6a. In a temperature range 30–90 °C, the value decreased from 151 cP to 53 cP, it maintained about 35% of its initial value at elevated temperature (90 °C).

3.1.5. Effect of shear rate

The plots of the apparent viscosities (η_{app}) versus shear rate for 0.5 g/dl of the tested HM-PAMs of the three groups in the brine solutions at 30 °C are shown in Fig. 7(a–c). The brine solutions for the three groups I, II and III exhibited the pseudoplastic and thixotropic behavior.

For the copolymers of group I in Fig. 7a, as the shear rate increased from 6 to 8.5 s^{-1} the η_{app} values decreased sharply from 220, 291 and 364 cP to 162, 216 and 270 cP for the PAM-Ia, PAM-Ib and PAM-Ic respectively, when, the shear

rate increased from 9 to 25 s^{-1} they decreased gradually to 127, 169 and 211 cP. Finally, the η_{app} values above the shear rate 25 s^{-1} tended to be constant due to the balance between the intermolecular association and disassociation. The values of η_{app} for the copolymers of group I missed about 45% of their initial values.

For the copolymers of group II in Fig. 7b, when the shear rate increased from 6 to 10.5 s^{-1} the values of η_{app} sharply decreased from 393, 444 and 484 cP to 267, 315 and 342 cP for the PAM-IIa, PAM-IIb and PAM-IIc respectively. They decreased gradually when the shear rate increased from 11 to 26 s^{-1} till they reached 177, 200 and 214 cP, above the shear rate 26 s^{-1} the values of η_{app} tended to be constant. They maintained about 45% of their initial values.

Fig. 7c shows the effect of shear rate on the η_{app} values of 0.5 g/dl brine solutions for the copolymer of group III, they behaved in a manner similar to the previous groups (I and II). When the shear rate increased from 6 to 11.5 s^{-1} the values of η_{app} sharply decreased from 288, 404 and 531 cP to 189, 270 and 360 cP for the PAM-IIIa, PAM-IIIb and PAM-IIIc respectively. Then, they decreased gradually when the shear rate increased from 11.5 to 27 s^{-1} till they reached 131, 174 and 235 cP, finally they tended to be constant above the shear rate 27 s^{-1} [26]. The η_{app} values reduced as the shear rate increased from 6 to 30 s^{-1} and the magnitude of reduction for the three copolymers was about 57% of their initial values.

While gradually reducing shear rate during the shear reversion process (drop) for the three copolymer groups (I, II and III), the values of η_{app} were almost equal to the primary viscosities (measured for the copolymers by increasing the shear rate (rise)) in the range of 6–30.5 s^{-1}. The obtained values of η_{app} for shear reducing process are very closely to the corresponding values of shear rising, the values may be up or down slightly but they completely recovered at 6 s^{-1} at the end of the process. These results imply that the intermolecular associations are reversible, and the copolymers do not degrade and their molecular structures are stable upon shearing which
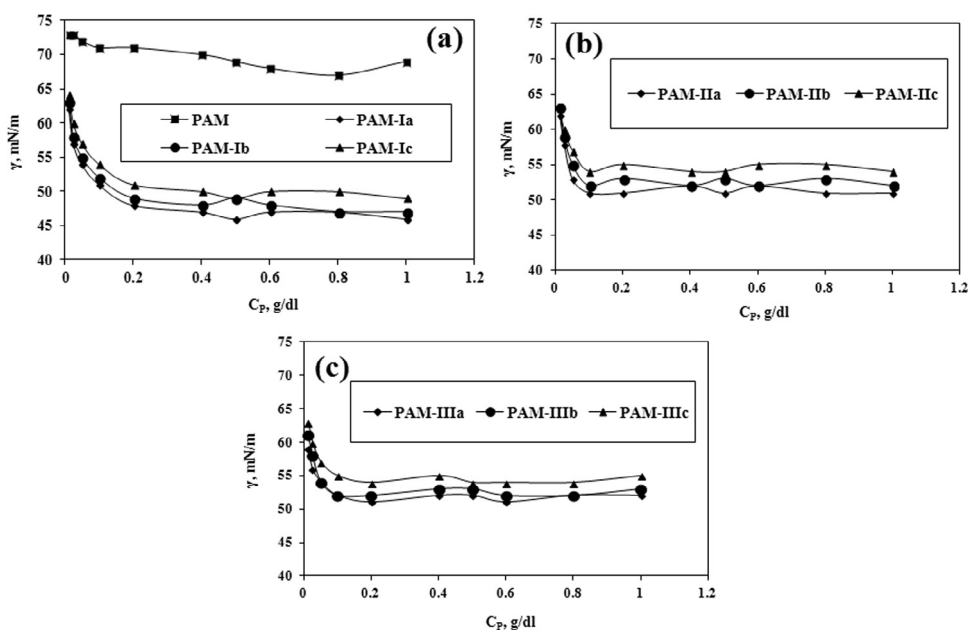
Figure 8 Surface tension (γ) versus concentration of (a) PAM and group I, (b) group II and (c) group III brine solutions at 30 °C.
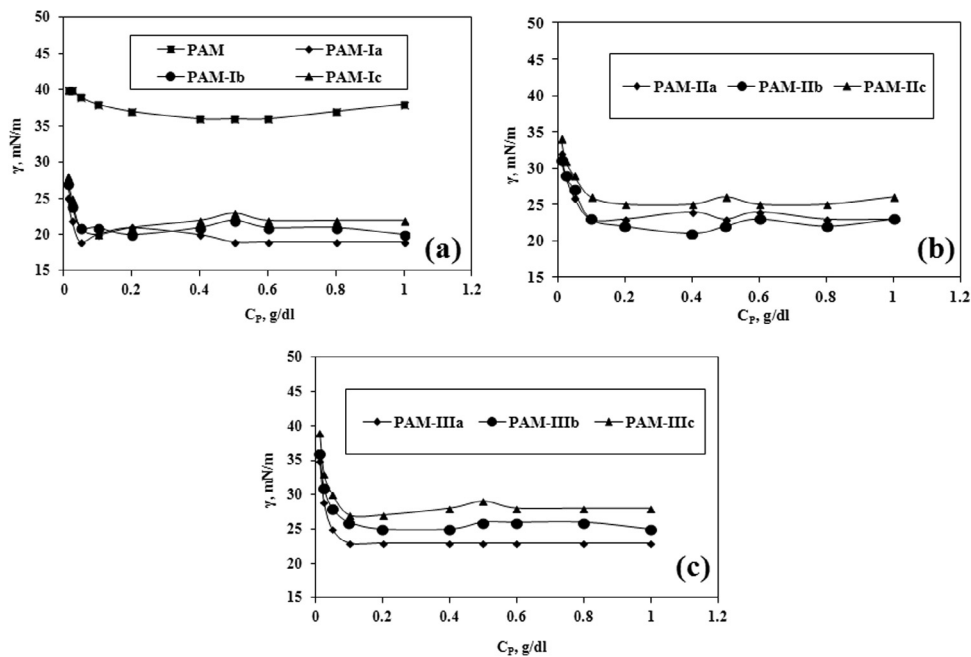
Figure 9 Interfacial tension (γ) versus concentration of (a) PAM and group I, (b) group II and (c) group III brine solutions at 30 °C.
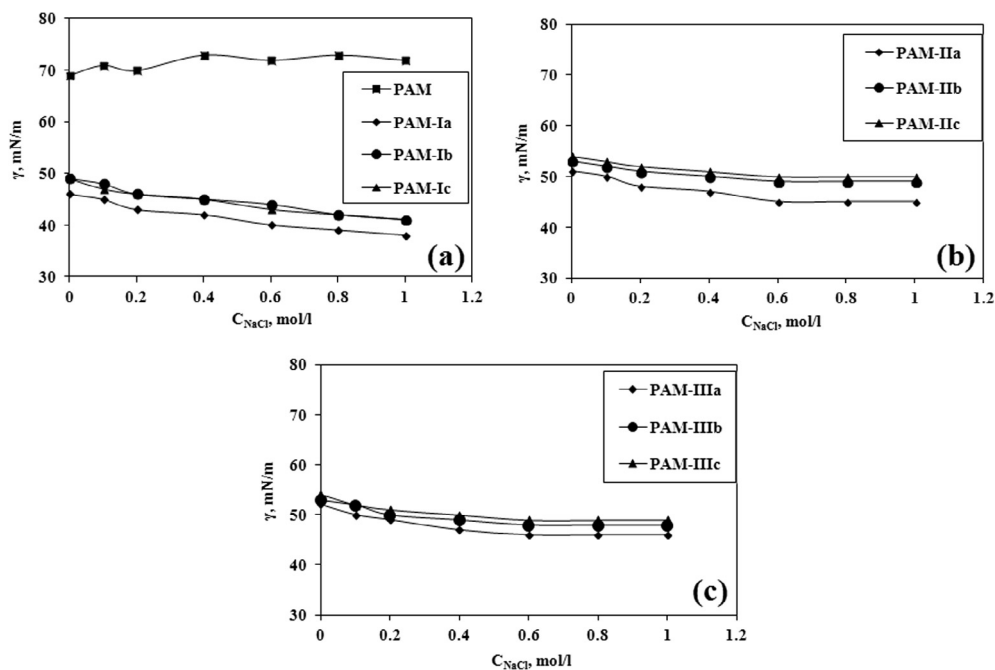

Figure 10 Effect of NaCl concentration on the surface tension (γ) of 0.5 g/dl brine solutions for (a) PAM and group I, (b) group II and (c) group III at 30 °C.

greatly enhances their use for enhanced oil recovery applications [25].

3.1.6. Effect of aging

The effect of time (aging) on the apparent viscosities (η_{app}) for 0.5 g/dl of the tested polymer and copolymers of the three groups (I, II and III) in the brine solutions at constant temperature (55 °C) for 45 days is listed in Table 2. The aqueous solu-

tions were used to fill ten 100 ml glass bottles. They were sealed placed in a thermostatted water bath (55 °C). The values of η_{app} for the polymer and the copolymer solutions were measured after different aging times. The η_{app} values obtained for the copolymers of group I maintained about 80% of their initial values after 45 days, while those for the copolymers of groups II and III maintained about 85%. Meanwhile the values of η_{app} for the PAM were also recorded in Table 2. They
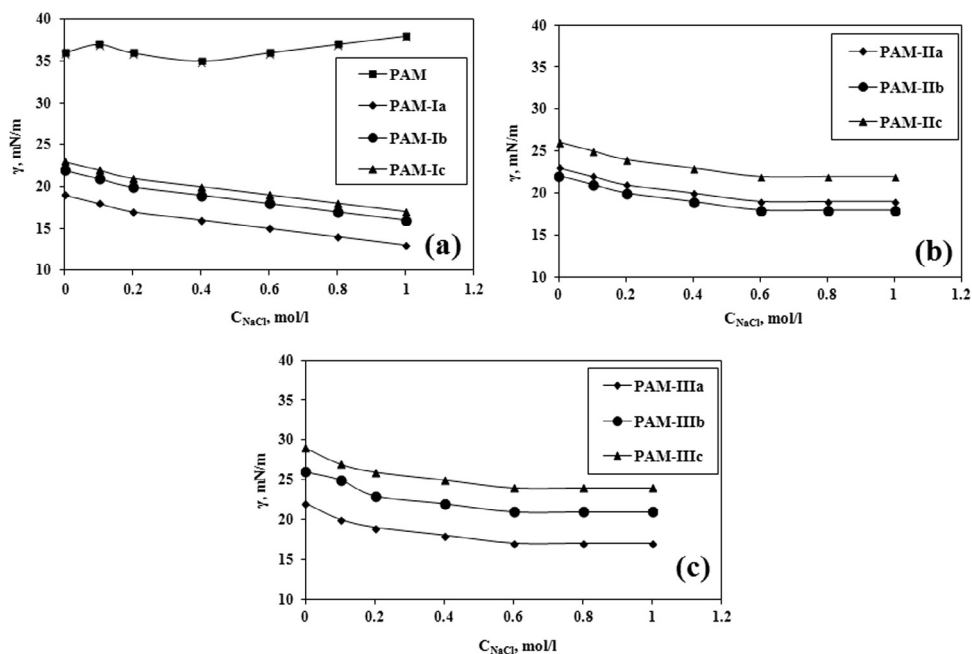
Figure 11 Effect of NaCl concentrations on the interfacial tension (γ) of 0.5 g/dl brine solutions for (a) PAM and group I, (b) group II and (c) group III at 30 °C.

Table 3 The stability of the crude oil emulsions formed by 0.5 g/dl polymer and copolymers brine solutions from 1 to 7 days at 30 °C.

Sample	Separated water/%						
	1	2	3	4	5	6	7
PAM	30	60	90	100	100	100	100
PAM-Ia	10	20	30	40	50	50	50
PAM-Ib	10	20	30	40	50	50	50
PAM-Ic	15	25	35	45	55	55	55
PAM-IIa	20	30	40	50	60	60	60
PAM-IIb	25	35	45	55	65	65	65
PAM-IIc	20	30	45	60	70	70	70
PAM-IIIa	15	30	35	50	65	75	75
PAM-IIIb	10	20	35	45	60	80	80
PAM-IIIc	10	15	25	35	70	85	85

lose about 25% of their initial values. These results show that the tested copolymers have good anti-aging properties in the brine solutions at 55 °C as a result of hydrophobic modification with the surfmers which incorporated into the copolymer backbone and hence, they should be used in the polymer flooding processes for enhanced oil recovery [25].

3.2. Surface, interfacial tensions and emulsification efficiency

The surface and interfacial tensions for the polymer (PAM) and the HM-PAMs were measured for concentration range from 0.01 to 1 g/dl at 30 °C and represented in Figs. 8 and 9. The copolymers of group I exhibited surface and interfacial activities better than those of the copolymers of groups II and III. This may be due to presence of the free carboxylic groups in their chemical structure comes from the copolymerizable parts (surfmers). The surface and interfacial tensions for

the PAM-Ia, PAM-Ib and PAM-Ic at 0.5 g/dl were 46, 49 ad 49 mN/m and 19, 22 and 23 mN/m respectively. The values obtained for the PAM-IIa, PAM-IIb and PAM-IIc were 51, 53 and 54 mN/m and 23, 22 and 26 mN/m. For the PAM-IIIa, PAM-IIIb and PAM-IIIc the surface and interfacial tensions corresponding to 0.5 g/dl were 52, 53 and 54 mN/m and 23, 26 and 29 mN/m respectively.

The effect of NaCl concentration on both surface and interfacial tensions of 0.5 g/dl brine solutions for the PAM and the tested HM-PAMs is illustrated in Figs. 10 and 11. For the copolymers of group I (PAM-Ia, PAM-Ib and PAM-Ic), as the concentration of NaCl increased from 0.1 to 1 mol/l, the surface and interfacial tensions obtained decreased gradually from 46, 49 and 49 mN/m and 19, 22 and 23 mN/m respectively to 38, 41 and 41 mN/m and 13, 16 and 17 mN/m. While, the values obtained for the copolymers of groups II and III, decreased gradually till 0.6 mol/l and above 0.6 mol/l they tended to be constant. For the PAM-IIa, PAM-IIb and PAM-IIc, the values of the surface tension decreased from 51, 53 and 54 mN/m to 45, 49 and 50 mN/m, the values of the IFT decreased from 23, 22 and 26 mN/m to 19, 18 and 22 mN/m. For the PAM-IIIa, PAM-IIIb and PAM-IIIc, the values of the surface tension decreased from 52, 53 and 54 mN/m to 46, 48 and 49 mN/m, the values of the IFT decreased from 22, 26 and 29 mN/m to 17, 21 and 24 mN/m.

In order to reduce the air-water surface tension and the oil–water interfacial tension for the tested copolymers, this led to enhance their emulsification efficiencies as illustrated in Table 3 and hence, improve their displacement efficiencies. The combination of thickening properties, surface and interfacial activities can be of great technological interest, especially in a number of important commercial applications such as enhanced oil recovery (EOR). The data showed that the emulsification efficiencies for the copolymers of group I were better than those for the copolymers of groups II and III. This may

be due to their better surface and interfacial activities. After 7 days, the copolymers PAM-Ia, PAM-Ib and PAM-Ic maintained 50%, 50% and 45% respectively, of the emulsified water, while the PAM-IIa, PAM-IIb and PAM-IIc maintained 40%, 35% and 30%, and the PAM-IIIa, PAM-IIIb and PAM-IIIc maintained 25%, 20% and 15%.

4. Conclusion

The solution properties for the tested copolymers were investigated in different aqueous media and their critical association concentrations (CAC or C^*) were determined. The dependence of the apparent viscosities for 0.5 g/dl brine solutions of the HM-PAMs on cation concentration, temperature ranging from 30 to 90 °C, shear rate ranging from 6 to $30.5 \, s^{-1}$ at 30 °C and aging time from 1 to 45 days were recorded. Their surface and interfacial tensions were measured for concentration range from 0.01 to 1 g/dl brine solutions at 30 °C and their emulsification efficiencies for 0.5 g/dl brine solutions were investigated for 7 days. Due to their resistance to added salts, elevated temperature, increasing shear rate, aging time and finally their emulsification efficiencies which increase the oil displacement effect, they can be used in enhanced oil recovery applications.

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