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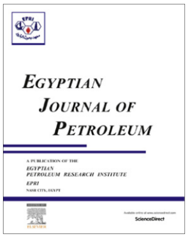

FULL LENGTH ARTICLE

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-

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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

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