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Effect of shearing actions on the rheological properties and mesostructures of CMC, PVP and CMC + PVP aqueous solutions as simple water-based drilling fluids for gas hydrate drilling

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ABSTRACT

The mesostructures of aqueous solutions (one simple type of water-based drilling fluids), with a kinetic hydrate inhibitor (polyvinyl pyrrolidone, PVP) or/and drilling fluid additive (sodium carboxymethyl cellulose, CMC), and their rheological properties after two shearing actions (600 r/min and 6000 r/min) were respectively investigated using a scanning electronic microscope (SEM) and a six-speed rotation viscometer, considering the different shearing actions imposed on drilling fluids during their circulation in the well. The results show (1) aqueous solutions with polymers (CMC, PVP and CMC + PVP) exhibit three different types of network framework (normally in the size of several to tens of micrometers), thin films + thin rods, globular particles + thin rods, and thin films + thin slices. Upon increasing the concentration of CMC or/and PVP, the thickness of the backbones and branches of the network framework increased, causing the volume of the pore space to decrease and the apparent viscosity and shear stress to increase. The tackifying effect of CMC was stronger than that of PVP, and the synergistic effect of CMC and PVP apparently increased the apparent viscosity and the shear stress. (2) With the shear rate increasing from 600 r/min to 6000 r/min, the apparent viscosities and shear stresses of these aqueous solutions decreased to some degree, and the four aqueous solutions of 0.75 wt% CMC, 1.5 wt% PVP, 0.75 wt% CMC + 1 wt% PVP, and 0.75 wt% CMC + 1.5 wt% PVP had relatively larger decreases in the apparent viscosity and the shear stress, which might result from changes in the spatial morphology of the network framework and the pore space, the spatial distribution and contents of the three different states of water, and the mobility of free water. The changes in the mesostructures might affect the local conditions of the heat and mass transfer in hydrate dissociation and formation in the annular space.

Introduction

Gas hydrates have long been considered by the scientific community to be the main hydrocarbon source for the coming century (Makogon, 2010). The estimated hydrate-related gas resources are 10^{13} and 20×10^{15} m^3 (at standard conditions) in permafrost and deep ocean sediments (Kvenvolden, 1998), respectively, where the temperature and pressure conditions are favorable for hydrate stability. Resources of gas hydrates account for 50% of the organic carbon in the earth (Kvenvolden, 1988), or twice the amount of conventional fossil energy (including both recoverable and non-recoverable) (Grauls, 2001). Major applications of hydrate research involve flow assurance, safety, energy recovery, gas storage/transportation, and climate change (Sloan, 2003).

Natural gas hydrates in sediments might cement grains, fill pores, or manifest as veins or nodules (Dai et al., 2004). Currently, the *in situ* permafrost or oceanic hydrate deposits of economic or technical interest in the world (Moridis et al., 2008) mainly include the Mallik Gas Hydrate Accumulation, the Eileen Gas Hydrate Accumulation (North Slope, Alaska, USA), the Messoyakha Field (West Siberia, Russia), the Nankai Trough (Offshore Japan), and the Oligocene Frio Formation (Gulf of Mexico). In China, similar drilling and coring studies have been performed in the South China Sea (Zhang et al., 2007) and in the permafrost of Qinghai (Lu et al., 2011). Optimum production methods vary for different hydrate reservoirs (Ning et al., 2010), but most of them cannot be performed without drilling. Distinct from drilling in conventional oil and gas reservoirs, drilling in gas hydrate-bearing sediments can

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more easily encounter hydrate phase transformation due to the low ambient temperature and high pressure conditions. One of these “industrial” gas hydrate-related geohazards that exist in both deepwater and permafrost-associated settings is shallow drilling and well-installation hazards that are encountered by wells targeting deeper horizons (“drilling through gas hydrate”) (Boswell et al., 2012). This type of geohazard experienced upon drilling includes not only gas hydrate plugging in the choke and kill lines, BOP, riser (Camero, 2000), valves, and pipes connecting to the surface and subsea equipments (Birchwood et al., 2005; Nimblett et al., 2005; Stow et al., 2012; Menon, 2014), but also deteriorating rheological properties, cutting carrying capacity and stability of aqueous solutions due to the gasification (Camero, 2000; Freij-Ayoub et al., 2007; Stow et al., 2012), and uncontrolled gas release in the annular space, blowout, fire, catastrophic well-site subsidence, disruption of casing cementing operation, gas leakage to the surface outside of the casing and casing collapse (Collett and Dallimore, 2002) due to *in situ* hydrate dissociation in the well or/and around the wellbore (Tan et al., 2005a; Birchwood et al., 2008; Khabibullin et al., 2011; McConnell et al., 2012) or drilling into deeper overpressured free gas below the hydrate stability zone (Birchwood et al., 2008; McConnell et al., 2012).

Recent studies mainly focused on the wellbore stability (Birchwood et al., 2005; Tan et al., 2005a; Freij-Ayoub et al., 2007; Khabibullin et al., 2011) and the inhibition of aqueous solutions i.e., the use of thermodynamic hydrate inhibitors (THIs) and low dosage hydrate inhibitors (LDHIs) of two types, kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs), such as NaCl and polyvinyl pyrrolidone (PVP) (Kumar et al., 2008; Masoudi and Tohidi, 2010; Yang and Tohidi, 2011). Partly because the gas generated by hydrate dissociation could relatively easily be controlled and not lead to serious safety problems through the use of normal drilling technologies, such as cooling and/or weighting drilling fluid and the addition of hydrate inhibitors (Birchwood et al., 2005; Freij-Ayoub et al., 2007; Khabibullin et al., 2011), there have been few studies on the effect of the mesostructure of water-based drilling fluids, the aqueous solutions formed by multiple polymers (such as viscosifiers, dispersants, or various inhibitors), on the heat and mass transfer of hydrate dissociation and reformation from the mesoscopic view, especially in the case of minor gas seepage around well bores in the upper part of deepwater and permafrost oil and gas exploration wells (Schofield et al., 1997; Collett and Dallimore, 2002; Nimblett et al., 2005; Peters et al., 2008; Boswell et al., 2009; McConnell et al., 2012). As the apparent difference in the behavior of the hydrate formation and dissociation between the bulk phase system and the porous media system is caused by the difference in the heat and mass transport (Sun and Mohanty, 2006), the spatial characteristics of the complex mesostructure of the aqueous solutions, including the network framework of polymer and the aqueous flowing part, play a very important role in studying the heat and mass transfer involved in hydrate phase transformation during drilling.

At present, the mesostructures of aqueous solutions are typically studied by scanning electron microscopy (SEM) (Zhong et al., 2011) with natural dry (Zhong et al., 2009a, 2010) or freeze-drying technology (Zhang et al., 1995; Zhu et al., 2005, 2006), environmental scanning electron microscopy (ESEM) (Feng et al., 2002; Zhong et al., 2009b), atomic force microscopy (AFM) (Hoare and Pelton, 2008; Zhong et al., 2008), cryogenic-transmission electron microscopy (Cryo-TEM) (Danino et al., 2001, 2003; Kuperkar et al., 2008), stimulated Raman scattering microscopy (SRS) (Freudiger et al., 2008), confocal laser scanning microscopy (CLSM) (Gaaloul et al., 2009) and freeze-fracture transmission electron microscopy (FF-TEM) (English et al., 2002; Mu et al., 2002; Luo et al., 2012). And other technologies such as differential scanning calorimetry (DSC) (Carenza et al., 1999; Baba et al., 2003), thermogravimetry (TG) (Vyaznikova et al., 1997; Neto et al., 2005), liquid chromatography (Baba et al., 2003), Fourier transform infrared (FTIR) (Ostrovskii et al., 1999) and ^{1}H NMR relaxometry (Carenza et al., 1999) were used to investigate the states and contents of water in many aqueous systems, such as membranes, hydrogels, and polymer solutions. According to the research results, the water in the aqueous solutions can be determined to be in three different states, freezable free water, freezable (loosely) bound water and non-freezable (strongly) bound water (i.e., freezing water and non-freezing water) (Tan et al., 2005b; Furushima et al., 2012). It is considered that the water states might have an important effect on conduction and convection heat and mass transfer in the pore space of the network framework of aqueous solutions.

Besides, during the whole circulation of the drilling fluid in a normal drilling process, the maximum shearing action normally occurs at the moment of drilling fluid flowing through the drilling bit due to the change in the flow area, with the nozzle equivalent shear rate of 6000 r/min, and the shearing actions in the inner hole of the drilling pipes and the annular space between the drill pipes and the wellbore are both weaker, with the equivalent shear rate less than or nearly equal to 600 r/min (Yan, 2006). These shearing actions also influence the mesostructure of the aqueous solutions to a certain degree, which results in changes in the rheological properties and characteristics of heat and mass transfer during gas hydrate formation and dissociation.

However, the mesostructures of aqueous solutions with kinetic hydrate inhibitors and the effect of the shearing action on the rheological characteristics of the aqueous solutions have not yet been probed at present. In this study, the rheological properties and mesostructures of aqueous solutions containing sodium carboxymethyl cellulose (CMC) and/or PVP (one simple type of water-based drilling fluids) were investigated by using a six-speed rotation viscometer and SEM. Two shear rates, 600 r/min and 6000 r/min, were selected to approximately represent the shearing actions that occur in the annular space between the drill pipes and the wellbore and at the moment of flow through the drilling bit, respectively. Based on these methods, the effect of the porous mesostructures of PVP or/and CMC aqueous solutions on hydrate formation and dissociation in the annular space was discussed. The results can help us understand the kinetics of hydrate dissociation and formation in the drilling system, the development of innovative KHIs, and the improvement of drilling operations in the gas hydrate-bearing sediments.

Experimental

Materials and instruments

The materials used include two polymers, CMC (with a viscosity of 800–1200 mPa·s, a typical drilling viscosifier) and PVP (K90, a classical kinetic hydrate inhibitor), and distilled water.

A low-speed mixer was used for dissolving the different polymers. A conventional high-speed mixer (0–11,000 r/min) for preparation of drilling fluids, with a spindle fitted with a single sine-wave impeller approximately 25 mm in diameter, was used for approximately achieving these two shearing actions of 600 r/min and 6000 r/min, respectively. A six-speed rotation viscometer was used for measuring the solutions' rheological properties. The mesostructures of the aqueous solutions were investigated by SEM.

Rheological property test and mesostructure study

In this experiment, there are three types of water-based aqueous solution, containing (1) CMC, (2) PVP, and (3) CMC + PVP.