Summary

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学　位　論　文　題　名

Exploring factors influencing the formation and stability of crude oil emulsion

（原油エマルジョンの形成および安定性に影響を与える要因に関する研究）

Emulsification plays a crucial role in various areas. However, undesirable emulsions, especially water-in-oil (W/O) emulsions, formed during crude oil production, transportation, processing, and stockpiling, become significant issues in the petroleum industry. Various studies have focused on evaluating the factors affecting emulsion stability and their mechanisms, which hardly explain the relationship with emulsion formation. Therefore, the main purpose of this study was to clarify the influences of different factors on both emulsion formation and stability as well as the corresponding mechanisms, which is beneficial for finding the ways to fundamentally avoid or reduce emulsification in petroleum.

Due to the functional groups of crude oils, pH and cations play significant roles in emulsion formation and stability from the view of water chemistry. Firstly, the transformation of emulsion types under various pH or cations were observed, and the stability of each corresponding emulsion was discussed subsequently. Meanwhile, the inapplicability of resolved water as a classical method to evaluate emulsion stability was discussed. The transformation from W/O/W emulsions to W/O emulsions happened for both crude oils under different pH and cation effects. The specific transformation process varied at different pH, and the difference in oil film thicknesses of both crude oil W/O/W emulsion was caused by the different viscosities as well as varied ratios of TAN/TBN. The W/O/W emulsion stability of both crude oils at different pH follows this order: neutral pH<low pH<high pH. The formation processes of emulsions formed in various cation brines were similar to those in pH6 brine while there are still differences caused between monovalent and divalent cations. The order of the particle size-determined W/O emulsion stability for both oils is as follows: high pH<low pH<neutral pH; $MgCl_2$<$CaCl_2$<NaCl. Combining the results of emulsion formation and resolved water, the feasibility of evaluating emulsion risk with resolved water was verified, which emphasized the importance of emulsion formation process for evaluating emulsion stability and risk as well. Finally, the mechanisms of the pH and cation effects on emulsion stability were proposed.

Crude oil as half of the subjects for emulsion formation plays a considerable role in determining the emulsion formation and stability. Also, crude oil acts as a mixture of polymers, and its

properties are significantly influenced by temperature, suggesting temperature can affect crude oil emulsions not only as an indirect factor but also as an energy-supporting resource. To further understand their influences on emulsification, the effects of temperature and crude oil properties on emulsion formation and stability was discussed. Regardless of temperature, W/O emulsion was transformed from W/O/W emulsion for various crude oils, and there was no big difference of W/O emulsion particle size. With increasing temperature, the particle size of W/O/W emulsion for most crude oils became smaller while oil film thickness became thinner. Meanwhile, the transformation rate was accelerated when increasing temperature. The most stable W/O/W emulsion was formed by crude oil with lowest viscosity at high temperature. The variation of resolved water percentage for different oils under temperature effect was consistent with emulsion formation process. For crude oil with a viscosity lower than 10 cp, high temperature can significantly reduce the W/O emulsion amount. The W/O emulsions can be destabilized by promoting water droplet coalescence at high temperature. Comparing the FTIR spectrum of crude oils and their W/O emulsions, it comes to the conclusion that the oxygen/nitrogen-containing functional groups contribute to forming crude oil emulsions. Hydrogen bonded O-H mainly dominates the W/O emulsion amount of crude oils, and hydrogen bonded N-H plays a non-negligible role as well.

Homogenization conditions including homogenization speed and time determine the shear intensity, which belong to the emulsion formation criteria for supporting effective energy. Homogenization conditions can determine the particle size of crude oil emulsions by varying energy. Therefore, it is vital to investigate and understand the effect of homogenization conditions on emulsion formation and stability of crude oils. The particle size and amount of W/O/W emulsions increased at high homogenization speed. W/O/W/O/W emulsion was formed in a certain speed range. High emulsion transformation speed was obtained at high homogenization speed, where the W/O emulsion was more stable. At low homogenizing speed, the multiple emulsion electrokenitics of crude oils were mainly controlled by TAN, while TBN had a significant influence at high homogenization speed. W/O emulsion stability was increased when increasing homogenization speed, which may be related to viscosity. Meanwhile, the water content of W/O emulsion increased. The amount of W/O emulsion for nine different oils increased with extending homogenizing duration. Homogenization time had a significant effect on W/O emulsion amount for crude oil with high molecular weight. Long homogenization duration can increase the W/O emulsion stability of crude oils. Furthermore, viscous solids considered as asphaltenes were precipitated for crude oil 6# from homogenization time extending to 60 min.

The outcomes obtained from this study would make up for the lack of observation data on W/O emulsion formation in the current research. The effects of various factors on emulsion formation and stability as well as the proposed mechanisms would shed light on the present knowledge of emulsification of crude oils. Furthermore, the ways obtained in this study including high pH, lowering shear rate, reducing shear duration, and increasing temperature based on oil types to reduce stable W/O emulsions may significantly contribute to the petroleum industry.