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CRUDE OIL ACID FRACTIONS AND THEIR HYDRATE PLUG INHIBITING PROPERTIES

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In petroleum production, gas hydrate formation may present a severe problem in the sense that hydrates may build up to large aggregates that are capable of plugging pipelines and platform equipment. However, in production systems containing crude oil it is observed that some systems are associated with high risk of plugging while others are not, when compared under the same physical conditions. These non-plugging crude oil systems are believed to contain natural inhibiting components, i.e. surface active compounds that have a strong affinity for the hydrate surface, which prevents growth and/or agglomeration of hydrate crystals. The hydrate morphology will thus be related to the state of wettability of the hydrates, which can span from water-wet to oil-wet. In systems where oil-wet hydrates are formed, they are present as small dispersed particles that are easily transported in the fluid (Høiland *et al.*, 2005a). Petroleum acids have previously shown inhibiting properties (Høiland *et al.*, 2005b). This behaviour can be attributed to adsorption of petroleum acids onto the solid hydrate surface, altering the surface of the particles into a more oil-wetted state.

To investigate the phenomenon of hydrate surface activity experimentally, we have isolated acid extracts from crude oils by means of ion exchange procedure (previously described by Mediaas et al. (2003)). The extracts have further been divided into sub-fractions by the use of liquid chromatography on SPE cyano columns, and both the acid extracts and their sub-fractions have been characterised by different analytical methods, i.e. FTIR, GPC, HPLC, LC-MS and GC-MS, with the purpose of identifying the hydrate surface active compounds, and to determine the acid sub-fractions in which they occur.

Furthermore, the ability of the crude oil acid extracts and their sub-fractions to alter the wettability of freon hydrates has been tested. This method is recently developed by Høiland *et al.* (2005a), and is based on phase inversion in crude oil/brine emulsions. Each of the acid sub-fractions is dissolved in a reference oil, which is a crude oil with initially high tendency to form hydrate plugs. The ability of the acid sub-fractions to interact with the freon hydrate surface is compared to the acid extract as a whole.

Some preliminary results are presented in Fig. 1, showing the measured points of phase inversions (i.e. the volume fraction of brine required to alter the system from oil-

continuous to water-continuous) in emulsions both with and without hydrates (Fig. 1 A), and the difference between them (Fig. 1 B). In general, a positive difference corresponds to oil-wet hydrates, whereas a negative difference corresponds to water-wet hydrates. Pairs of measurements are shown before and after adding acid extracts from two crude oils B4a and B4c to the reference oil (concentration 6500 ppm). An increase in the value of the phase inversion point is observed for the systems with added acids extracts. This behaviour is attributed to formation of more oil-wet hydrates, and hence lower risk of formation of hydrate plugs.

The results from emulsion tests will be correlated to the characterised acid profiles of the oils. Further work on sub-fractions of acid extracts will be presented, and indications of the more hydrate surface active acids will be given.

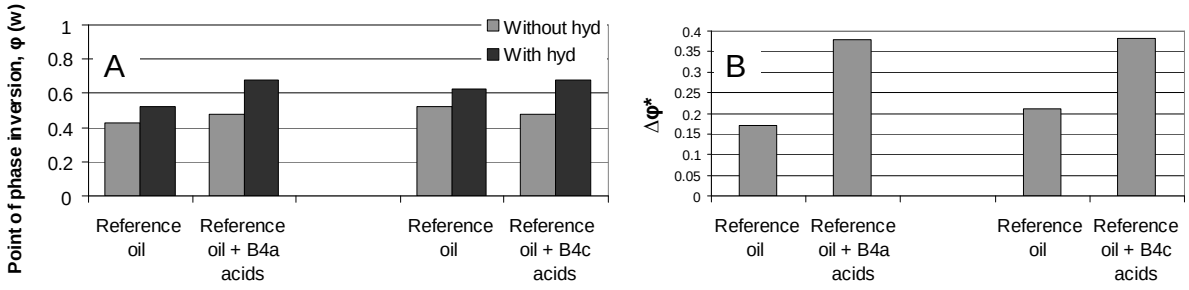

Figure 1. Points of phase inversion for some systems of crude oil/brine with and without added acid extracts.

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