PHASE BEHAVIOUR OF COLLOIDAL CRUDE OIL SYSTEM

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The formation of colloid aggregates was monitored by measuring flocculation points of solutions of crude oils and oil fractions. With regard to concentration, flocculation points of crude oil solutions can be calculated analogous to flocculation points of polymer solutions. As criterion for the metastability of colloidal crude oil systems the Flory-Huggins interaction parameter can be used. The interaction parameter depends on the difference of solubility parameters between the surface of the colloid particles and the dispersion medium fraction of the oil. The critical interaction parameter of flocculation was found to be $\chi_{crit} = 0.62 \pm 0.04$.

INTRODUCTION

Detailed knowledge about the forming mechanism of the colloid disperse phase and about the factors responsible for stabilizing resp. precipitating the disperse phase is of major importance in production, transportation, and refining of petroleum.

The reason for the formation of a colloid disperse phase is the great difference in interaction forces among the petroleum components. Asphaltenes are only partially soluble under these conditions and form crystallites that are solvated to form colloid disperse primary particles of about 3 nm diameter. Investigations have shown [1] and [2] that the ratio of the volume of the colloid particles to the volume of asphaltenes is between 2.5 and 3.5. This solvation shell around the asphaltenes is greater than the average content of resins. Decreasing metastability of the colloid disperse system effects the aggregation of primary particles and finally the precipitation of colloid disperse phase.

The influence of different factors on the metastability of colloid disperse crude oil systems can be investigated determining flocculation points.

1 EXPERIMENTAL

The flocculation points were determined by a titration method. A precipitant is added at a constant rate to the solution of the petroleum product under intensive stirring. The titration is monitored by a light intensity meter. After flocculation onset the intensity decreases and the maximum of the curve is defined as the flocculation point.

2 RESULTS AND DISCUSSION

The concentration influence on flocculation points of petroleum was found to be analogous to the dependence of polymer solutions. Equation (1), derived for polymers by Elias and Gruber [3], is valid:

$$\log \Phi_{pre} = \log \Phi_{crit} - k \log c_{pol} \qquad (1)$$

Φ_{pre} : Volume fraction of precipitant at the flocculation point;
c_{pol} : Concentration of polymer at the flocculation point;
Φ_{crit} : Critical volume fraction of precipitant at a polymer concentration of $c_{pol} = 1\ g\ cm^{-3}$;
k : Constant, dependent on molecular mass of polymer.

To value the influence of solvent-precipitant pairs the solubility parameters of the solvent-precipitant mixtures at the flocculation points and of the petroleum fractions were calculated.

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The most important results are:

- Independent of applied solvents the solubility parameters of the solvent-precipitant mixtures at the flocculation points increase with the solubility parameter of the applied precipitant.
- The higher the solubility parameter of the petroleum fraction, the higher the solubility parameter of the solvent-precipitant mixture at the flocculation point.

Considering the behaviour of polymer solutions the following relations can be used for the interpretation: the solubility of polymers is determined by a critical value of the Flory-Huggins interaction parameter that can be calculated according to equation (2) [4], neglecting the entropy term:

$$\chi_{crit} = 0.5\,(1 + m^{-0.5})^2 \qquad (2)$$

χ_{crit} : Critical value of the Flory-Huggins interaction parameter;

m : Ratio of molar volumes of polymer and solvent.

Consequently, the reason of different values of solubility parameters at the flocculation points applying n-alkanes as precipitant is their different molar volumes.

On the other hand the Flory-Huggins interaction parameter is a function of the solubility parameters of solvent and solute [5]:

$$\chi = \frac{V_s}{RT}\left(\delta_{sl} - \delta_s\right)^2 \qquad (3)$$

V_s : Molar volume of solvent;

δ_{sl} ; d_s : Solubility parameter of solute; of solvent.

As a criterion for metastability we can express:

$$\chi \le \chi_{crit} \qquad (4)$$

In colloid disperse petroleum systems the limiting value of metastability should be determined by the particle volume of petroleum colloids. In equation (3) the solubility parameter at the surface of the colloid particle towards the dispersion medium δ_{part} has to be used. With attention to the gradient in solubility parameter across the solvation shell $\Delta\delta$ it is valid:

$$\delta_{part} = \delta_{as} - \Delta\delta \qquad (5)$$

δ_{as} : Solubility parameter;

$\Delta\delta$ values in the range of 0.4 to 1.4 (MJ $m^{-3})^{0.5}$ were obtained by comparing flocculation points of solutions of asphaltenes and original residues.

On the base of these relations, that are only valid for more or less unpolar solvent-precipitant pairs, we found:

$$\chi_{crit} = 0.62 \pm 0.04$$

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Final manuscript received in January 1997