Adsorption of asphaltenes and resins on organic and inorganic substrates and their correlation with precipitation problems in production well tubing

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The solute–solid adsorption isotherms (SSA) of asphaltenes and resins were measured using the inorganic fraction (97% SiO_2) of the deposit that plugged the tubing of a production well as an inorganic adsorbent. In other experiments, Ceuta asphaltenes and the product (HA) of heating them at 350°C for 11 h were used as organic adsorbents in heptane, toluene and heptane–toluene at 26°C. Ceuta and Furrial asphaltenes on the inorganic substrate resulted in multilayer formation (L-3 type adsorption) whereas a Cerro Negro sample gave simple Langmuir-type adsorption. A possible correlation between these results and the tendency of the asphaltenes to precipitate from the crude oils is suggested. Saturation, multilayer formation and pore penetration were apparent in the SSA experiments for the system resins–heptane–asphaltenes. SSA results for the system resins–heptane/toluene–HA were consistent with the steric stabilization theory of colloidal dispersions. Adsorption of aggregates or micelles of asphaltenes was apparent in both the organic and the inorganic substrates.

(Keywords: asphaltenes; adsorption; deposit formation)

The precipitation of asphaltenes in oil well production tubing is an important practical as well as theoretical problem, owing to its negative impact on the petroleum industry. Haskett and Tartera[1] analysed the problem of asphaltene deposits in the Hassi Messaoud field and found that the tops of such deposits correlated with the bubble points of the wells. Hirshberg et al.[2] studied the problem of asphaltene solubilization using a modification of the treatment of Flory and Hildebrand[3] and concluded that pressure and composition are important parameters in the prediction of asphaltene precipitation. In agreement with Haskett and Tartera, their model predicted that the solubility minimum occurs at the pressure corresponding to the bubble point; it also predicted an increase in solubility with pressure above the bubble point as a result of an increase in the solubility parameter of the crude. Below the bubble point the solubility increases again owing to the separation of low-molecular-weight gases.

The solubility of asphaltenes in crude oil is probably related to the stability of their colloidal aggregates or micells. It has long been proposed that asphaltene aggregates are stabilized by resins adsorbed on their surface[4–6], and much research has been done which confirms this hypothesis. Katz and Beu[7] reported colloidal particles < 6.5 nm in diameter. Winniford[8] measured molecular weights of 500 000. Dickie and Yen[9] as well as Herzog et al.[10] reported macrostructures for the asphaltene micelle, and Andersen and Birdi[11] and Sheu et al.[12] have reported critical micelle concentration

(CMC) values for asphaltenes under different conditions. Leontaritis and Mansoori[13] have proposed that the flocculation of asphaltenes is the result of desorption of resins from the micelle surface when the crude oil is diluted with a low-molecular-weight hydrocarbon such as pentane or heptane.

The tendency of asphaltenes to form aggregates should parallel their capacity for multilayer formation on a solid surface. A study of the solute–solid adsorption isotherms (SSA) of asphaltenes and resins on inorganic and organic surfaces was therefore undertaken. The relation of the results to the precipitation and dispersion of asphaltene micelles is discussed.

EXPERIMENTAL

Asphaltenes and resins

The asphaltenes were obtained by addition of 60 volumes of *n*-heptane to a 1:1 v/v mixture of crude oil and toluene, as described earlier[14]. The precipitate was filtered and Soxhlet-extracted with *n*-heptane for 4 days, after which it was found to be completely free of resins. Evaporation of the *n*-heptane from this extraction procedure yielded the resins used in this work.

The above samples were obtained from three different crude oils: Cerro Negro (13% asphaltenes, 66% resins, 8.3°API), Ceuta (20% asphaltenes, 26% resins, 11°API) and Furrial (10% asphaltenes, 21.3°API). The H/C

Table 1 Inorganic content and SARA analysis of the organic content of well deposits found in the Ceuta field

Sample	Inorganic content (%)	Organic analysis (%)			
		Saturates	Aromatics	Resins	Asphaltenes
1	50	10	3	22	65
2	11	6	0	21	73
3	16[a]	5	2	16	76
4	1	5	2	15	78

[a] Sample used as inorganic adsorbent in this work

atomic ratios of the asphaltenes were 1.14 for Cerro Negro and 0.9 for Ceuta. The resins obtained from the Ceuta crude were the only ones used in this study.

Adsorbents

The inorganic adsorbent was collected from the incrustations or scale deposited on the production tubing of the Ceuta well. This was powdered in a laboratory mill, Soxhlet-extracted (chloroform) and sieved to 53–74 μm. X-ray characterization showed the adsorbent to be 97% SiO_2 with a surface area of $4.8\ m^2\ g^{-1}$. The chloroform was evaporated and the organic residue was analysed by automatic thin-layer chromatography with flame ionization detection.

The organic or asphaltene adsorbent (HA) was prepared from Ceuta asphaltenes by heating at 350°C for 11 h under nitrogen, extraction with toluene to remove any soluble oil and drying under vacuum for 2 h. This material was then powdered to 53–74 μm.

Adsorption experiments

The concentration of adsorbed asphaltenes or resins was determined by u.v. spectrometry (400 nm) as described elsewhere[15]. Solutions in the range 0.02–10 g l^{-1} were prepared using 10 ml of toluene shaken with 200 mg of adsorbent for 24 h in a water bath at 26°C.

Solute–solid adsorption isotherms (SSA) on the inorganic solid were determined with the three asphaltenes and with the resins of the Ceuta crude oil, and those on the organic solid with the Ceuta samples only (asphaltenes and resins).

Near changes in slope of the isotherms the results were subject to more scatter than in other regions. Averages of three or more measurements were therefore taken near these changes. The other points are averages of at least two determinations.

Surface tension measurement

Surface tensions were measured on toluene solutions of Ceuta asphaltenes (0.5–10 g l^{-1}) using a tensiometer by the Wilhelmy plate method at 22°C.

RESULTS

The results of the analyses of the deposits are presented in *Table 1*. The inorganic content varies from 50 to 1% and in all cases the asphaltenes and resins together account for >87% of the organic fraction. From these results and those discussed below, it appears that adsorption on inorganic as well as on organic materials is important in the formation of deposits that result in the plugging of tubing and other production facilities.

The SSA of Cerro Negro asphaltenes is shown in *Figure 1*. There is no significant increase in adsorption above 1 g l^{-1}, and the adsorption curve is of the L or Langmuir type, suggesting the absence of cooperative adsorption[16]. Multilayer or other solute–solute interactions are not revealed by the present experiments. The apparent surface saturation concentration is 2.75 mg g^{-1}, corresponding to an equilibrium concentration of 0.8 g l^{-1}. L-type behaviour has been reported elsewhere for different asphaltenes and inorganic adsorbents[15,17,18]. It should be mentioned that the Cerro Negro crude does not present any problems related to asphaltene precipitation.

The SSA of the Ceuta asphaltenes is shown in *Figure 2*. Beyond the L-type curve observed below 0.5 g l^{-1} the adsorption again rises, increasing with the solution equilibrium concentration. This behaviour has been termed L-3 and is usually attributed to multilayer formation[19].

Similar results were found for Furrial asphaltenes (*Figure 3*), with no evidence of saturation at the high concentrations examined. It should be noted that the adsorption on the inorganic surface is a small fraction of the total; this could imply that the observed inflections are due to the adsorption of asphaltene aggregates or micelles.

To check whether the equilibrium concentration at the inflection points in the curves of *Figures 2* and *3* corresponds to a CMC, the surface tension of the corresponding toluene solutions was measured. However, a constant value of 28 mN m^{-1}, scarcely different from that of toluene (27.5 mN m^{-1}), was found when the concentration was varied.

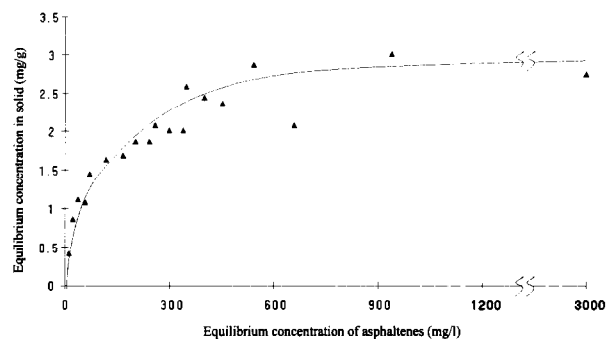Both Ceuta and Furrial crude oils present serious

Figure 1 Adsorption of Cerro Negro asphaltenes on the inorganic material. Solvent, toluene; temperature, 26°C
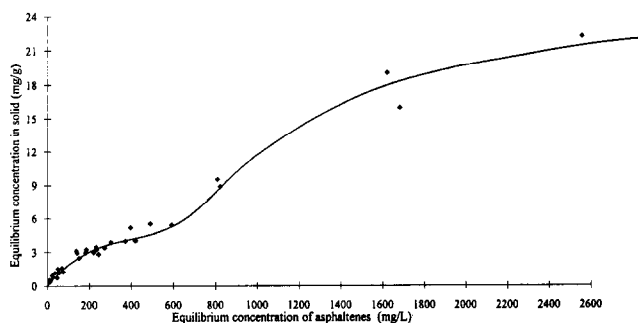

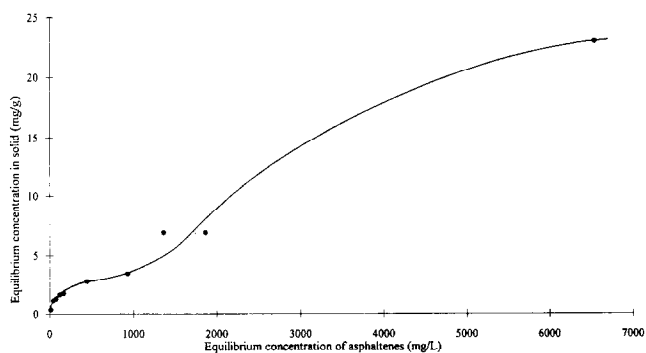Figure 2 Adsorption of Ceuta asphaltenes on the inorganic material. Solvent, toluene; temperature, 26°C

Figure 3 Adsorption of Furrial asphaltenes on the inorganic material. Solvent, toluene; temperature, 26 C
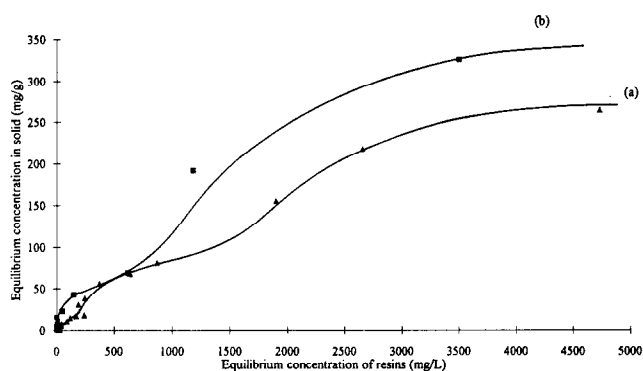

Figure 4 Adsorption of Ceuta resins on asphaltenes (a) and heated asphaltenes (b). Solvent, heptane; temperature, 26°C

problems of asphaltene precipitation in field production facilities. The results shown above are consistent with the strong solute–solute interactions and aggregate formation resulting from such behaviour. It would be of interest to investigate whether those asphaltenes such as Cerro Negro that do not lead to serious precipitation problems will in general produce L-type adsorption curves.

Some SSA experiments were carried out with the Ceuta resins dissolved in toluene. However, their adsorption on the inorganic solid was insignificant, suggesting behaviour comparable with that for the solvent.

Figure 4 shows the SSA of Ceuta resins on asphaltenes and heated asphaltenes (HA). Both curves are complex, indicating that multilayer adsorption and other phenomena may be present. At low concentration the heated asphaltene (HA) shows H-type (high affinity) behaviour; that is, at $<14\,\mathrm{mg\,l^{-1}}$ of added sample all the resin present is adsorbed. Since the HA sample was expected to be a more adsorbent solid, this result is not surprising.

In *Figure 4*, the initial section of curve (a) could be associated with an L-type curve[16,19] and hence its first infection suggests a saturation which corresponds to $\sim 18\,\mathrm{mg\,g^{-1}}$, located between 160 and 240 mg l^{-1}. A second plateau is observed between 600 and 1000 mg l^{-1}, corresponding to about four times the saturation concentration and probably due to multilayer formation; after which the concentration of adsorbed resins rises continuously, suggesting that they penetrate within the asphaltene pores.

Curve (b) in *Figure 4* cuts the vertical axis at 14 mg g^{-1} and then rises to $\sim 70\,\mathrm{mg\,g^{-1}}$, suggesting multilayer

formation in this interval. Above 70 mg g^{-1} the behaviour is similar to that found in the asphaltene experiments. This curve is compared in *Figure 5*, as (a), with two others using 3:1 heptane–toluene (b) and pure toluene (c) as solvents. As expected, the adsorption of resins decreases on going from heptane to toluene.

The adsorption of Ceuta asphaltenes on HA is illustrated in *Figure 6*. At low solution equilibrium concentration the adsorption is at least 10 times that observed for the inorganic material, indicating a considerably higher affinity of the asphaltenes for a surface of similar structure to their own. Since the inflection point is $\sim 80\,\mathrm{mg\,g^{-1}}$ it is likely that multilayer formation occurs at solution concentrations $<1000\,\mathrm{mg\,l^{-1}}$. As discussed below, this point could be a consequence of the formation and adsorption of micelles.

DISCUSSION

As mentioned above, whereas Ceuta and Furrial asphaltenes are capable of forming multilayers, it appears that the Cerro Negro sample does not do so. These findings strongly suggest that the chemical potential (μ) of the former samples is higher, which is consistent with their tendency to precipitate from the crude oil under field operations. Thus, although in principle their precipitation could be a consequence of factors such as asphaltene content, crude composition, pressure, temperature, etc., it is believed that the main reason for this phenomenon lies in the asphaltenes themselves. For
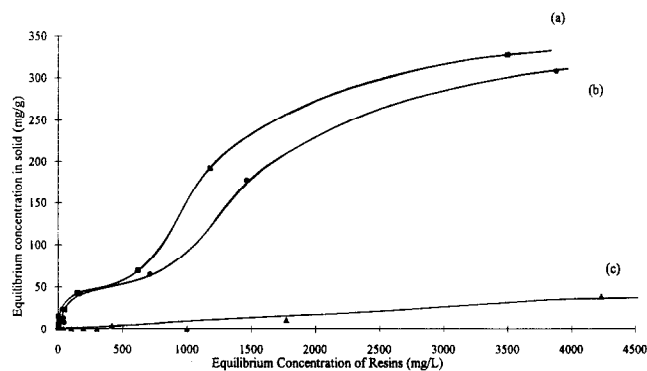

Figure 5 Adsorption of Ceuta resins on heated asphaltenes. Solvent: (a) heptane; (b) 3:1 heptane–toluene; (c) toluene; temperature, 26°C
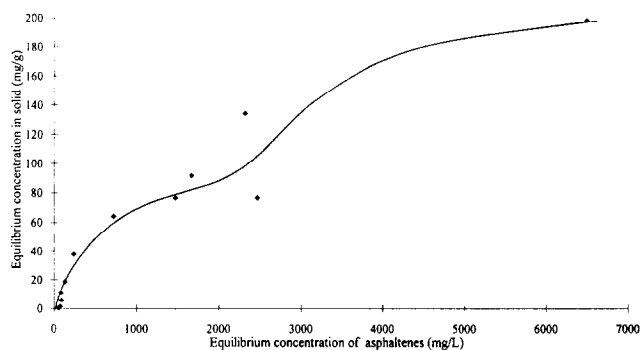

Figure 6 Adsorption of Ceuta asphaltenes on heated asphaltenes. Solvent, toluene; temperature, 26°C

example the H/C ratios of both Ceuta and Furrial are significantly smaller than that of Cerro Negro asphaltenes (see Experimental). Confirmation of these findings should be obtained in the near future.

The changes in slope observed at low asphaltene concentrations (see *Figures 1–3*) could be due to the normal saturation of the inorganic surface. However, when the adsorbent is HA this possibility no longer exists, because in this adsorption inverval the surface is already a multilayer. Thus it is likely that the inflection in the curve could indicate the adsorption of micelles.

Menon and Wasan[20] associated the change in slope of the adsorption of shale oil asphaltenes on sodium montmorillonite with the formation of micelles. These authors reported a CMC value of $0.55 \, \mathrm{g \, l^{-1}}$ in a 1:1 v/v mixture of *n*-heptane and toluene.

According to the results in *Figures 4* and *5* the resins are capable of forming multilayers on an asphaltene surface in heptane and 3:1 heptane–toluene. In toluene, their adsorption is very low. These results are consistent with the steric or osmotic mechanism of flocculation as proposed by Flory and Krigbaum[21] and others[22] for polymers adsorbed on the surface of colloidal particles. In this mechanism, the stabilization of the colloidal dispersion depends on the balance between the interaction of polymers adsorbed on different particles (a negative contribution to the total free energy) and two repulsive or positive contributions arising from the volume of intersection of the two approaching particles and the increase in concentration of polymer in such a volume. The repulsive terms prevail when the enthalpy of the polymer–solvent interaction is significantly more negative than that corresponding to the interaction between two polymer molecules. In such cases the colloidal dispersion will be stable.

The resin multilayer illustrated in *Figure 4* arises from the adsorption of resins from the solution on to resins already adsorbed on the asphaltene surface. In a real dispersion of asphaltenes the flocculation will occur after the interaction between the resins adsorbed on different particles of asphaltenes as they approach each other.

Another point of interest results from the comparison of *Figures 4* and *6*, which shows that the asphaltenes–

asphaltenes interaction (adsorption) is far more important than the one between asphaltenes and resins. This has been a mater of speculation in the past.

The above results could be extended to crude oil as follows: in the presence of the inorganic material found in oil, the Ceuta and Furrial asphaltenes adsorb on to the surface of the organic material, leading to the formation of multilayers. The resins are then adsorbed on the asphaltenes, leading to a floc that is dispersed or flocculated depending on whether the interaction of the adsorbed resins with the medium (crude) is stronger or weaker than with themselves. In this way the inorganic material acts only as a nuclei for flocculation.

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