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Temperature Dependence of Complexation Processes in Asphalt
and Relevance to Rheological Temperature Susceptibility

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INTRODUCTION

It has been established that asphalts or petroleum distillation residues are not homogeneous, but micellar based systems (1). The composition of the micelles is controversial and is considered to involve aggregates of mainly asphaltenes or complexes of asphaltenes with other high molecular weight components. The approach described in this paper was developed using the latter concept with interchanges of components between the micelles and the continuous phase that are highly temperature dependent. Mechanisms are proposed that describe how the consistency of asphalt cements changes with varying temperatures. These mechanisms involve component interchanges between the micelles and the continuous phase in asphalt.

The viscosity of the complete asphalt system is caused by the major contributions from both the micellar and continuous phases. The continuous phase viscosity depends on that of each component, in particular those of high viscosity. If the micelles were spheres with no interaction then their contribution to the viscosity of the asphalt would be small. However, it is known (2) that there must be considerable bridging between the asphaltenic micelles resulting in various degrees of cross-linked networks. This can be explained by the fact that the micelles are considered to have polar groups on their surfaces which associate with polar groups on neighbouring micelles to form loose networks. These networks contribute markedly to the viscosity of asphalt cements.

The micelles are considered to be complexes with the most polar components,

namely the asphaltenes at their cores. Other less polar components are deposited on top of the more polar ones with the least polar components located at the extreme exterior surface of the micelle, as shown in Fig. 1. The continuous phase contains large amounts of the less polar components and they are major contributors of viscosity. The following colloidal model is proposed to explain resistance to changes in viscosities due to temperature changes and rheological temperature susceptibilities.

The less polar (and possibly higher molecular weight) high viscosity components can be interchanged between the micellar complexes and the continuous phase. On cooling, they are gradually withdrawn from the continuous phase due to complexation with the micelles in order of their degree of polarity. Therefore, as the cooling proceeds, the components undergoing complexation and also those that remain in the continuous phase become less and less polar. Thus, the surface of the micelles becomes less polar and this results in loosening of the bridging between micelles. Both the removal of the polar components and loosening of the micellar network result in the resistance to viscosity increases during cooling. These processes are shown in Fig. 2. On warming, viscosity decrease is resisted by the reverse processes.

This model can also be explained with the following equations:



$$K_p = \frac{[Pol]_{\text{micellar}}}{[Pol]_{\text{continuous}}} \quad 2)$$

$$K_p = f(T) \quad 3)$$

where [Pol] represents the exchangeable components and K_p is the equilibrium constant. One way to demonstrate this model would be to show that the degree of complexation is highly temperature dependent, for example, at the extremes of the service temperatures experienced by asphalt pavement. The effect of temperature on precipitation from alkane solutions was chosen to prove that the degree of

complexation is temperature dependant. While precipitation with alkanes will not include all micelles/complexes, increased complexation should increase the amounts of precipitate. The procedure that was followed is similar to the standard method of determining pentane insolubles with two modifications: lower levels of dilution (solvent to sample ratio) were used; and the precipitates could not be washed because this would remove much of the complexed materials.

The effect of temperature on the determination of asphaltenes has been reported in the literature (3-6). Andersen and Budi (3) report a maximum precipitation in the region of 30°C. Mitchell and Speight(6) report that the amount of precipitated asphaltenes in Athabasca bitumen increases with temperatures up to 70°C, and this is related to the decrease of the Hildebrand solubility parameter with temperature. Among these referenced works, very little attention has been given to the material that precipitates with the asphaltenes. This material is removed and lost during the washing step required in the pentane insoluble determination method. Some of the materials that are removed by washing are the components that are complexed on the surface of the micelles.

The temperature susceptibility of asphalt cement is a function of the equilibrium distribution, K_p , of components between the micelles and the continuous phase, as shown in equation 1. Since temperature alters the equilibrium, it is the change in K_p with temperature that determines the temperature susceptibility, as shown in equation 3. The affinity of the distributing components for the micelles is dependent upon the chemical nature of the asphalt cement.

EXPERIMENTAL

Asphalt Samples

- Esso 85/100 asphalt cement containing 16.1% asphaltenes (heptane insolubles).
- PetroCanada 85/100 asphalt cement containing 17.9% asphaltenes (heptane

insolubles).

Determination of Temperature Susceptibility

The penetration index was used to measure temperature susceptibility. The equation used to calculate the penetration index is given as (7):

$$PI = (20 - 500A) / (50A + 1) \quad 4)$$

where A is the slope obtained from the plot of logarithm (base 10) of the penetration in dmm with temperature in centigrade degrees.

Effect of Precipitation at Various Temperatures

The initial experiments consisted of thorough dispersion of the asphalt samples in pentane at room temperature. These mixtures were kept at the desired temperature overnight, then were filtered quickly through No.1 Whatman filter paper. The pentane was allowed to evaporate from both the precipitate on the filter paper and from the filtrate. The precipitate and liquids were then weighed. In another pilot experiment the mixtures were centrifuged at the desired temperatures and samples were taken of the supernatant liquids. The solvent was evaporated from the supernatant liquid and the amount precipitated was determined by the difference between the asphaltic material in the centrifuged liquid and the original mixture.

In later experiments, the mixtures were stirred at the desired temperatures for 6 h and allowed to remain at the desired temperature overnight. Samples were then taken with a syringe fitted with a 0.45 μ m membrane filter to retain suspended solids. The amounts precipitated were determined by difference with the original mixtures.

DISCUSSION

Precipitation at Different Temperatures

The results from the initial temperature precipitation and filtration experiments are shown in Tables 1 and 2. These precipitates were not washed to retain the complexed components with the asphaltenes at the expense of retaining solvent and non-complexed asphalt components. The amounts of precipitate obtained at 25°C for the *Esso* 85/100 asphalt at different concentrations did not significantly differ significantly. However, at 0°C the amount of precipitate for the 20% concentration was almost twice that observed at 25°C. For the 5% concentration at 0°C, there is also a large increase in the amount of precipitates but considerably less than for the 20% mixture.

The filtrates from these experiments were analyzed by the ASTM D4124 method and are reported in Table 3. The filtrates obtained at the lower temperatures were enriched in saturates but depleted in polar aromatics compared with those obtained at the higher temperature. This is consistent with the model of micelle complexation described earlier since the saturates are expected to be the least complexed with the asphaltene micelles and the polar aromatics are expected to be among the most strongly complexed.

It is apparent that the reproducibility of the above experiments is poor, therefore the centrifugation method was used, the results of which are shown in Table 4. There is evidence of changes due to temperature but the reproducibility of these experiments is also inadequate. It is considered that the reproducibility is limited by difficulties in the transfer of components from the continuous phase to the precipitate and thus the time required to attain equilibrium is long. Both the duration of the experiment and the absence of stirring or mixing may have prevented replication of results. Further, the size of the micelles may vary with temperature and sample, with considerably different rates of diffusion to and from the surface of the complexes (8).

The results of experiments where longer times and stirring were used are shown in Tables 5 and 6. For the Esso 85/100 asphalt cement, the amount of precipitate varied directly with dilution, as would be expected due to greater addition of alkanes per unit of asphalt cement, and indirectly with temperature. The reproducibility of this experiment was best at 30% concentration and worst at 10%. For the PetroCanada 85/100 asphalt, the amount of precipitate varied directly with dilution but the effect of temperature was greater at higher asphalt concentrations (lower dilutions).

These results, particularly those in Tables 5 and 6, demonstrate that the degree of complexation is highly temperature dependent. This supports the model's prediction of higher complexations at lower temperatures, and is the basis for predicting that changes in viscosity with temperature can be controlled by controlling the complexation of the micelles. Further study is necessary to demonstrate this effect, perhaps by adding both polar and non-polar oils and residues to asphalt cements to relate blending, to control the degree of complexation, and temperature susceptibility.

CONCLUSIONS

A model involving a colloidal system and temperature dependent complexation processes has been proposed to explain the mechanisms in asphalt that determine its rheological temperature susceptibilities. It has been shown experimentally that these temperature dependent complexation processes do occur.

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Table 1 - Results of preliminary precipitation experiments, 25°C,
Esso 85/100 asphalt cement, pentane solvent

| | | | | | | |
|---------------------|-------|-------|-------|-------|------|-------|
| Concentration, Wt % | 20 | 20 | 10 | 10 | 5 | 5 |
| Sample | 1 | 2 | 1 | 2 | 1 | 2 |
| Precipitate, Wt % | 32.8 | 30.7 | 37.0 | 35.7 | 33.2 | 33.5 |
| Solubles, Wt % | 68.3 | 70.7 | 64.3 | 65.7 | 66.4 | 67.1 |
| Total, Wt % | 101.1 | 101.4 | 101.3 | 101.4 | 99.6 | 100.6 |

Table 2 - Results of preliminary precipitation experiments, 0°C,
Esso 85/100 asphalt cement, pentane solvent

| | | | | |
|---------------------|-------|-------|-------|-------|
| Concentration, Wt % | 20 | 20 | 5 | 5 |
| Sample | 1 | 2 | 1 | 2 |
| Precipitates, Wt % | 59.0 | 63.1 | 43.2 | 40.6 |
| Solubles, Wt % | 43.2 | 45.0 | 62.3 | 64.8 |
| Total, Wt % | 102.2 | 108.1 | 105.5 | 105.4 |

Table 3 - Effect of temperature on filtrate composition (ASTM D4124)

| | | | | |
|----------------------------|------|------|------|------|
| Concentration, Wt % | 20 | 20 | 5 | 5 |
| Temperature, °C | 25 | 0 | 25 | 0 |
| Saturates, Wt % | 14.2 | 17.4 | 14.7 | 16.5 |
| Naphthenic aromatics, Wt % | 41.3 | 42.0 | 45.6 | 50.8 |
| Polar aromatics, Wt % | 45.5 | 40.8 | 37.9 | 35.2 |

Table 4 - Effect of temperature on precipitation, centrifugation experiments

| Concentration, Wt % | 5 | 20 |
|------------------------------|------------------------------|------------------------|
| Precipitation at +20°C, Wt % | 38.3, 27.0, 23.8, 27.0 | 22.1, 35.1 |
| Precipitation at -20°C, Wt % | 40.6, 35.1, 32.8, 40.7, 38.9 | 49.7, 27.6, 55.5, 54.8 |

Table 5 - Precipitation from stirred mixture of Esso 85/100 asphalt cement in pentane

| Concentration, Wt % | 10 | 20 | 30 | 40 |
|------------------------------|------------|------------|--------------|------------|
| Precipitation at 20°C, Wt % | - | - | 6.03 | 4.85 |
| Precipitation at 0°C, Wt % | 18.4, 17.0 | 13.55 | 8.40 | 5.13 |
| Precipitation at -20°C, Wt % | 16.4, 34.3 | 17.25 | 11.20, 10.77 | 8.67, 8.20 |
| Precipitation at -35°C, Wt % | 26.5, 36.8 | 23.7, 29.1 | 14.8, 14.7 | 8.18 |

Table 6 - Precipitation from stirred mixture of Petro-Canada 85/100 asphalt cement in pentane

| Concentration, Wt % | 30 | 30 | 40 | 40 |
|------------------------------|-------|-------|------|------|
| Precipitation at 20°C, Wt % | 8.63 | 8.50 | 3.65 | 2.72 |
| Precipitation at 0°C, Wt % | 10.03 | 9.13 | 4.92 | 4.65 |
| Precipitation at -20°C, Wt % | 11.17 | 11.23 | 7.18 | 7.10 |
| Precipitation at -35°C, Wt % | 15.0 | 14.5 | 11.1 | 10.7 |

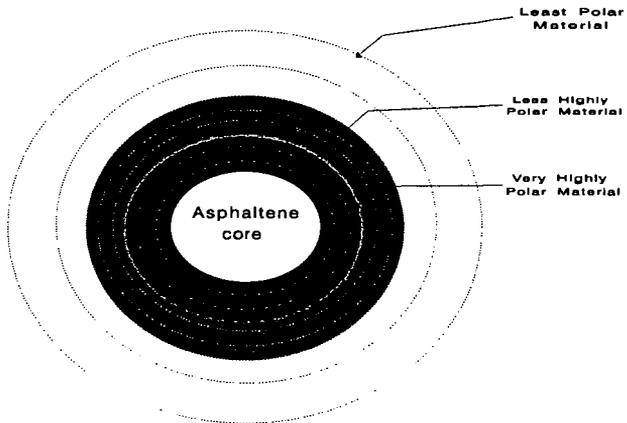


Fig. 1 - Diagram of micelle showing asphaltene core and decreasing polarity of surrounding material from core to surface.

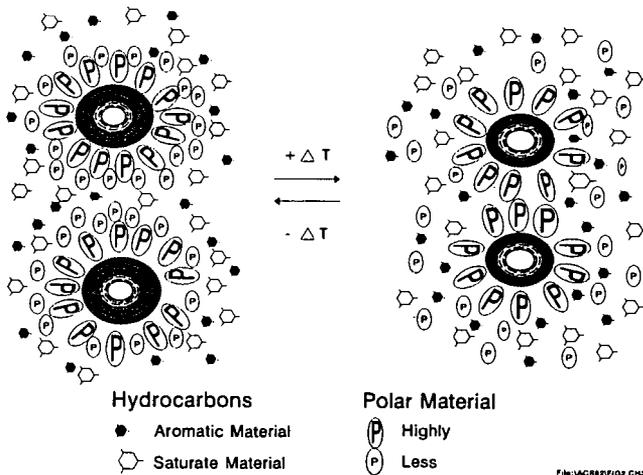


Fig. 2 - Diagram showing component change with temperature in a two phase asphalt system