

# KINETIC PROPERTIES OF EMULSIFIED ASPHALTS

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## ABSTRACT

The effect of shear on the non-Newtonian viscosity of emulsified asphalts is presented. Measurement of the viscosity behavior of several emulsions by rotational viscometer, shows that the viscosity decreases under constant shear until an equilibrium viscosity is attained. A first-order kinetic model is used to analyze the viscosity data and to obtain rate constants for each emulsion. Based on their rate to attain an equilibrium viscosity, emulsions were ranked as follows: CRS-2R > CMS-2P > CRS-1P ~ CMS-2s > CRS-2 > CRS-2P > HFRS-2 > HFRS-2P. From the rate constants, relaxation times were obtained for each emulsion. Anionics had the longest relaxation times compared to the cationic emulsions. The steady-state viscosity  $\eta_{ss}$ , initial viscosity  $\eta_0$ , and the viscosity  $\eta$  at any time were used to obtain the rate constants. The cationic emulsions attained their equilibrium viscosity at a faster rate than the anionics. This is attributed to the different type of interaction between droplets and aggregate microstructure. The different rates are consistent with the observation that pumping and stirring (shearing) of emulsions in the field result in a reduction of their viscosity.

## Introduction

Emulsified asphalts were characterized by rotational viscometry for the first time in 1948 showing how their flow properties were dependent on shear rate (1). Rotational viscometry has been proposed as a quality assurance tool (2). Recent work shows that the equilibrium viscosity of emulsified asphalts, cationic and anionic, can be determined with good repeatability by rotational viscometry (3). The rotational viscometry method performed at 50 °C, 50 RPM and with spindle 21 (method 50-50-21) has been proposed as a test method for emulsions including using emulsion equilibrium viscosities for road emulsion specifications (4,5). The emulsions studied were thixotropic and attained an equilibrium viscosity at 50 RPM, 50 °C and after about 20 minutes. Different emulsion grades differed in their rates to attain a steady-state viscosity. Emulsified asphalts have a microstructure of aggregate droplets (flocs) that under steady shear breaks into individual droplets. Quantitative description of shear thinning behavior of emulsions in terms of microstructure breakdown (deflocculation) has been described elsewhere (6,7). A kinetic model has been used to interpret the thixotropic behavior

of latex solutions, polymer melts, and heavy mineral oil (8). The reduction in viscosity was modeled by proposing a simple 'reaction' scheme:

Unbroken microstructure -----> broken microstructure,

that for discussion to follow is rewritten as



**AM** represents a microstructure consisting of linkage between emulsion droplets and the right-hand side **A + M** represents the 'broken linkage between these emulsion droplets. This results in a reduction of emulsion viscosity. In this study one shear rate and temperature is used to demonstrate the usefulness of the kinetic model to determine emulsion rate constants.. In practice, it is observed that the viscosity of emulsified asphalts under constant pumping or stirring (shearing) is reduced. It is shown that by using rotational viscometry and analyzing the viscosity data using a simple kinetic model it is possible to quantify the decrease in viscosity at some shear rate and temperature. The practical application of these results can be used to predict the flow behavior of emulsified asphalts in process equipment.

### **Experimental**

Viscosity experiments were conducted on a Brookfield RVDVIII+ equipped with a thermo cell for temperature control. A stainless steel sample chamber and spindle #21 were used for all experiments. The spindle was selected such that the torque was greater than 10% according to Brookfield data gathering criteria. Sample preparation was according to ASTM D 244 (9). Cationic emulsions used were CRS-2P (polymer modified rapid set), CMS-2S (medium set with solvent), CRS-2 (rapid set unmodified), CRS-2R (a polymer modified rapid set), CMS-2P (a medium set polymerized), CRS-1P (polymer modified), HFRS-2P (polymer modified) and HFRS-2 (unmodified) are high float anionic emulsions. Measurements were conducted at 50°C and at a shear rate of 50 RPM. Emulsions had a mean asphalt residue content of 65%. A 3000-RPM laboratory centrifugal pump (Little Giant, 1/20 HP) was used to pump a cationic emulsion and to demonstrate the drop in viscosity with process equipment and viscosities measured with a Saybolt Furol viscometer.

### **Description of Rheograms**

Typical rheograms for CRS-2P and CRS-2 are shown in Figures 1 and 2 respectively. Figure 1 shows three viscosity regions described as, microstructure breakdown, equilibrium viscosity, and emulsion breaking. Microstructure breaking under constant shear results in a decreasing viscosity until an equilibrium viscosity is obtained. Emulsion breaking occurs at long shear times and is not the subject of this paper. Figure 2 is a CRS-2 rheogram and shows good repeatability. This viscosity profile is typical for all emulsions studied.

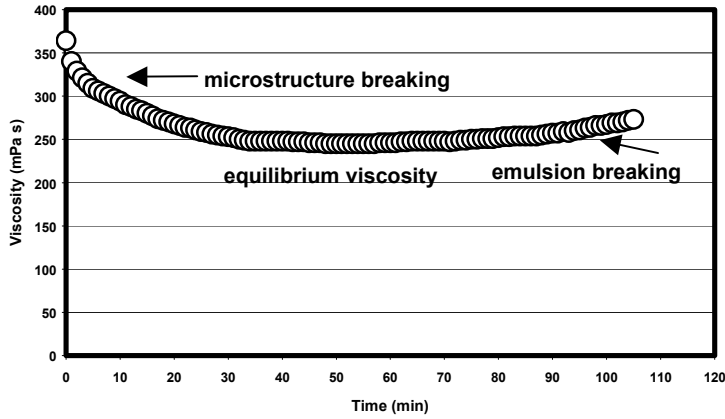


Figure 1. CRS-2P time-dependent viscosity at 50°C and at 50 RPM showing the three viscosity regions.

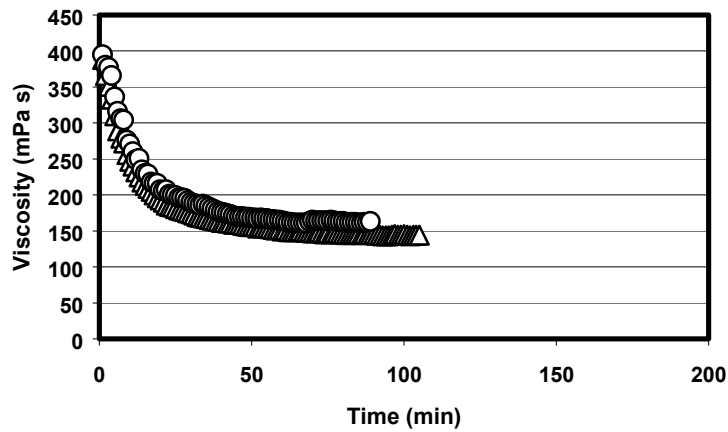


Figure 2. CRS-2 duplicate runs showing repeatability at 50°C and 50 rpm

### Kinetic Model

The viscosity behavior for thixotropic substances as discussed before is modeled using a reaction kinetics approach. The ‘break up’ of aggregate microstructure AM to give A and M with rate constant  $k$  is represented as



and the rate of disappearance of AM is proportional to the amount of AM,

$$d \frac{[AM]}{dt} = -k[AM]_t \quad (2)$$

where  $[AM]$  represents the ‘concentration’ of the aggregate AM. The solution to the first-order rate law given in (2) is the integrated form shown in (3)

$$\ln[AM]_t = -kt + \ln[AM]_o \quad (3)$$

The change in viscosity with time was followed at 50 RPM and 50 °C. Because the viscosity is proportional to the concentration equation (3) is expressed in terms of a measured property of the emulsion:

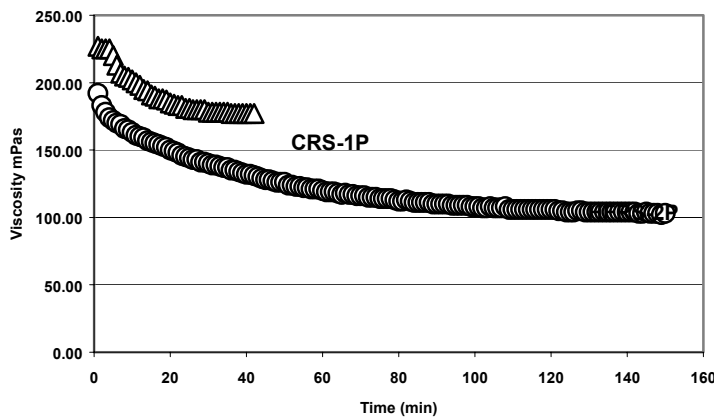
$$\ln[\eta - \eta_{ss}] = -kt + \ln[\eta_o - \eta_{ss}] \quad (4)$$

where  $[\eta - \eta_{ss}]$  is the ‘concentration’ of  $[AM]_t$  at any time and  $[\eta_o - \eta_{ss}]$  is the initial concentration  $[AM]_o$

In the kinetic model,  $\eta_o$  is the original viscosity (minimum broken microstructure) at initial shearing of the emulsion,  $\eta_{ss}$  is the steady-state viscosity (maximum broken microstructure) at some constant shear rate, and  $\eta$  is the apparent viscosity at any time (a mixture of broken and unbroken microstructures). A plot of  $\ln[\eta - \eta_{ss}]$  against time is expected to be a straight line if the emulsion microstructure breakdown obeys first-order kinetics as postulated. Alternatively, since viscosity is directly related to stress these experiments can also be considered as some form of stress relaxation under a constant strain rate. An equilibrium stress is obtained after some time. From the reduction in shear stress a relaxation time ( $\tau$ ) can be obtained from equation 5 (10) In this study the relaxation time is obtained from the rate constant as shown in equation 6.

$$g = g_o e^{-\frac{t}{\tau}} \quad (5)$$

$$\tau = \frac{1}{k} \quad (6)$$

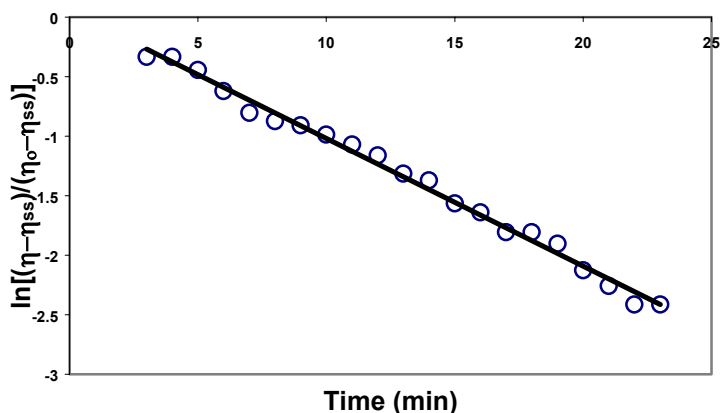


**Figure 3. Viscosity comparison for CRS-1P and HFRS-2P at 50 C and 50 RPM**

## Results and Discussion

In Figure 3 is shown two extremes of emulsion thixotropic behaviour. A CRS-1P is compared to an HFRS-2P emulsion. The CRS-1P polymer modified cationic emulsion attains a steady-state viscosity significantly faster than the HFRS-2P polymer modified anionic emulsion. The eight emulsions studied show similar viscosity profile as seen in these examples and as described before.

Figure 4 is a typical example of the integrated first-order plot (equation 4) where the slope is the rate constant from equation 4. All plots were linear and with correlation coefficients equal to 0.99 except for CMS-2s, which was 0.97. Summaries for rate constants are given in Table 1, including relaxation times and R squared values.



**Figure 4. Typical semi-log plot to obtain rate constant from viscosity-time data.**

The CRS-2R unmodified cationic emulsion had the fastest rate constant compared to the HFRS-2P anionic emulsion. As shown in Table 1, the cationics as a family of emulsion had the fastest rates. The CRS-2P had the slowest rate within the cationic types. This may be attributed to the fact that the CRS-2P emulsion had the highest degree of polymer modification compared to the other cationics, which may lead to more interaction between emulsion droplets and hence a more strongly linked microstructure. For the two anionics, the polymer modified HFRS-2P had a lower rate constant than the unmodified HFRS-2. This again may be attributed to stronger interaction between droplets of HFRS-2P compared to the unmodified HFRS-2. It has been claimed that these anionics, which in the literature are called ‘high float’ emulsions, have a gel structure. It is postulated that these ‘high float’ anionics have a ‘tighter’ aggregate microstructure (more elastic) therefore their breakdown requires more time to attain a steady-state viscosity. The rate trend for the cationics is probably related to the different emulsifier types, which in turn have an important role in determining the nature of the interaction between the droplets. This in turn determines the type of aggregate microstructure that influences the rheological properties of these emulsions.

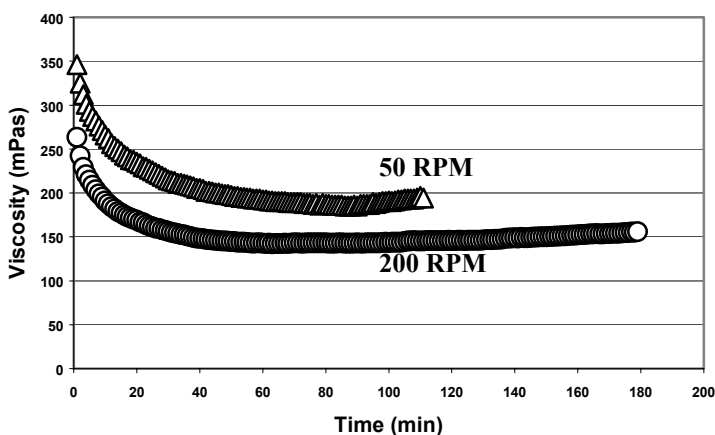
**Table 1. Summary of rate constants and relaxation times.**

Emulsions	$K$ ( $\text{min}^{-1}$ )	$R^2$	$\tau$ relaxation time (min)
CRS-2R	0.131	0.99	8
CMS-2P	0.106	0.99	9
CRS-1P	0.090	0.99	11
CRS-2	0.082	0.99	12
CMS-2S	0.078	0.97	13
CRS-2P	0.059	0.99	17
HFRS-2*	0.031	0.99	32
HFRS-2P	0.025	0.99	40

Figure 5 shows the effect of a higher shear rate on the viscosity behavior at 50°C for the HFRS-2P anionic emulsion. At 200 RPM the equilibrium viscosity is attained sooner than at 50 RPM. Table 2 shows the results obtained for the HFRS-2P anionic emulsion by using the first-order kinetic model analysis. The rate constant is changed by two and half times when the shear rates is changed by a factor of four. This is another example of how this kinetic model can be used quantitatively to obtain rate constants from the viscosity behavior of emulsions measured by rotational viscosity at other shear rates. The quantitative characterization of emulsion flow properties can be of use to predict their behavior in process equipment and other field applications where their rheological properties are of fundamental importance.

**Table 2. Effect of shear rate on rate constant.**

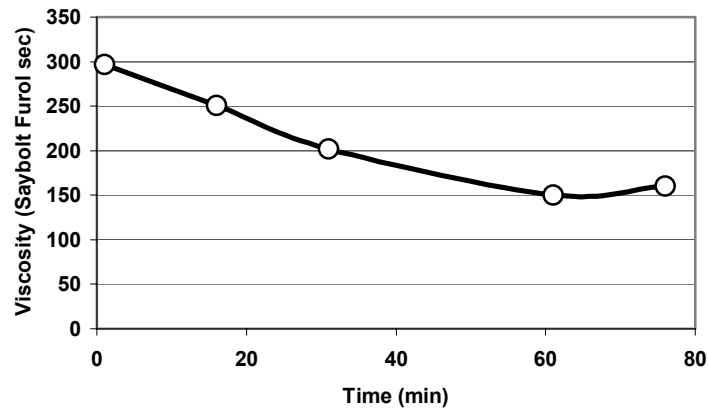
Emulsions	$k_1$	rpm	$\tau$ relaxation time
HFRS-2P	0.025	50	40
HFRS-2P	0.063	200	16



**Figure 5. Effect of shear rate on the viscosity of HFRS-2P at 50 and 200 RPM.**

## Practical Application

An experiment was run on a five-gallon sample of CRS-2P product at 50°C and 3000 RPM to determine the effect on emulsion viscosity using a laboratory centrifugal pump. The emulsion was recirculated for one hour and the viscosity measured every 15 minutes. The result of this experiment is shown in Figure 6. The Saybolt Furol viscosity was taken until an equilibrium viscosity was reached for the recirculated emulsion. The viscosity behavior was similar to what was observed in the more controlled rotational viscometry experiments.



**Figure 6. Viscosity reduction of CRS-2P emulsion using a 3000 rpm centrifugal pump**

## Conclusions

Analysis of the viscosity data obtained from rotational viscometry for eight different emulsions show that the thixotropic behavior of emulsified asphalts follow first order kinetics. The rate constants obtained are related to the different grades of emulsion, where the anionic emulsions show the lowest rate constants. The rates constants are related to the rate of microstructures breakdown (deflocculation) that is unique for each emulsion grade. The microstructure of each emulsion influences their rheological properties that is important to their use in process equipment and field application. This preliminary study have shown that the anionics studied attain their equilibrium viscosity at a much slower rate that the cationics. This is attributed to a more strongly-linked aggregate microstructure for the anionics high float compared to the cationics.

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