

ASPHALT COMPATIBILITY TESTING USING THE AUTOMATED HEITHAUS TITRATION TEST

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ABSTRACT

The Heithaus titration test or variations of the test have been used for over 35 years to predict compatibilities of blends of asphalts from different crude sources. Asphalt compatibility is determined from three calculated parameters that measure the state of peptization of an asphalt or asphalt blend. The parameter p_a is a measure of the peptizability of the asphaltenes. The parameter p_o is a measure of the peptizing power of the maltenes, and the parameter P , derived from p_a and p_o values, is a measure of the overall state of peptization of the asphalt or asphalt blend. In Heithaus' original procedure, samples of asphalt were dissolved in toluene and titrated with n-heptane in order to initiate flocculation. The onset of flocculation was detected either by photography or by spotting a filter paper with a small amount of the titrated solution. Recently, an "automated" procedure, after Hotier and Robin,¹ has been developed for use with asphalt. In the automated method UV-visible spectrophotometric detection measures the onset of flocculation as a peak with the percent transmittance plotted as a function of the volume of titrating solvent added to a solution of asphalt. The automated procedure has proven to be less operator dependent and much faster than the original Heithaus procedure. Results from the automated procedure show the data to be consistent with results from the original, "classical" Heithaus procedure.

INTRODUCTION

Historically, asphalts have been classified into gel-type asphalts and sol-type asphalts.² Gel-type asphalts usually are characterized by non-Newtonian rheological behavior, relatively low variation of viscosity with temperature, and low ductility. Sol-type asphalts exhibit more Newtonian rheological behavior, are highly temperature susceptible, and are more ductile. The two classifications represent extremes, and most asphalts are of intermediate nature. Sol-type asphalts have been designated as compatible asphalts, while gel-type asphalts have been designated as incompatible asphalts.

The terms "compatible" and "incompatible" (or sol-gel) arose from what became known as the colloidal model of asphalt structure. This model considers asphalts to be dispersions of what are termed "micelles," consisting of polar, aromatic molecules in viscous oils. The degree to which the so-called "micelles" form extended gel structures, unstable to heat and shear, will determine the relative degree of incompatibility. In a compatible asphalt, the dispersed materials are well peptized by the oils (maltenes), either because the dispersed materials are small in amount and/or tend not to form strong associations, and/or because the solvent effectively disperses the "micelles." In an incompatible asphalt, associations are more extensive and are not so efficiently peptized by the solvent.

The colloidal model has been subjected to much criticism in recent years. The principal objection is that there is no direct evidence for "micellar" structures, either classical or inverse, in asphalts. The term "micelle," which implies existence of a separate phase with distinct boundaries, may be inappropriate when applied to asphalts. Recently, a microstructural model of asphalt structure has been proposed.³ In this model, associations of polar molecules of varying sizes are considered to be dispersed in a polar moiety composed of less polar, relatively small molecules. No distinct phase boundaries are believed present. Nevertheless, the concept of compatibility as a measure of mutual miscibility of different chemical components of asphalts is useful. Compatible asphalts do differ from incompatible asphalts in their physical properties and in pavement performance. Highly compatible asphalts are not necessarily good to achieve all important performance related properties and likewise for low compatible asphalts. This makes compromises in compatibility necessary for optimum overall pavement performance.

Asphaltenes are solid materials which precipitate when asphalts are treated with solvents such as n-pentane, n-hexane, n-heptane, etc. Maltenes are the components of asphalts not precipitated by n-alkane solvents. Asphaltenes are more aromatic than maltenes and contain more heteroatoms. Thus intermolecular interactions are more extensive in asphaltenes than in maltenes. This is reflected in the greater molecular weights of asphaltenes compared with maltenes.⁴ In the colloidal model of

asphalt structure, asphaltenes are believed to correspond to the dispersed materials and maltenes to the solvent. Therefore, asphaltenes will be mainly responsible for the internal structure of asphalts and will dominate many physical properties.³ Thus the amount of asphaltenes in an asphalt is a rough measure of compatibility. Compatible asphalts generally have smaller amounts of asphaltenes than incompatible asphalts. Oxidative aging of an asphalt will decrease compatibility by formation of polar molecules, which cause increasing associations and result in more asphaltenes. The ease with which asphaltenes are dispersed is highly dependent on the dispersing power of maltenes, which are also a contributing factor to asphalt compatibility. The best known measurement of compatibility of asphalts that takes all the above factors into account is the Heithaus^{6,7} test. In this test, flocculation behavior of asphaltenes is measured. The method is tedious and does not work with waxy asphalts, so a study of asphaltene flocculation behavior to develop an improved compatibility test was implemented.

EXPERIMENTAL

What has been termed the classical Heithaus titration procedure is described below. Four 1.0 g samples of a test asphalt are placed into four 125 mL Erlenmeyer flasks. To the four flasks are added amounts of 1.0, 2.0, 4.0, and 6.0 mL toluene, respectively. After dissolution of the asphalt is completed, the flasks are immersed in a water bath maintained at 25°C (77°F) for 30 minutes. The flasks are titrated with 1.0 mL aliquots of n-heptane. After each addition of n-heptane, the contents of the flask are stirred for several minutes, and then inspected to observe if flocculation has taken place. Flocculation is detected by transferring a drop of the solution to a filter paper with a glass rod. The development of two rings on the filter paper signifies the onset of flocculation. Heithaus parameters p_a , p_o , and P are calculated from the flocculation ratio and the concentration, respectively. The flocculation ratio (FR) and concentration (C) are calculated as:

$$FR = \frac{V_s}{V_s + V_T} \quad (1)$$

$$C = \frac{W_a}{V_s \cdot V_T} \quad (2)$$

where V_s is the volume of solvent, V_T is the volume of titrant required to initiate flocculation and W_a is the weight of the asphalt. In the classical Heithaus procedure, FR values are calculated for solutions of asphalt at various concentrations, and concentration values are plotted versus flocculation ratio values. The x and y intercept values FR_{max} and C_{min}^{-1} extrapolated from the FR vs. C line are used to calculate Heithaus parameters p_a , the peptizability of asphaltenes; p_o , the peptizing power of maltenes; and P , the state of peptization of the asphalt, as follows:

$$p_a = 1 - FR_{max} \quad (3)$$

$$p_o = FR_{max}(C_{min}^{-1} \cdot 1) \quad (4)$$

$$P = \frac{p_o}{1 - p_a} \quad (5)$$

The automated Heithaus procedure differs somewhat from the classical procedure. In the automated procedure three to five samples of a test asphalt are weighed into 30 mL vials with Teflon sealed caps. Contrasting with the classical procedure, in which the weight of asphalt is held constant and the volume of solvent is varied, the automated procedure uses different weights of asphalt from sample to sample, and the volume of solvent is held constant. To the vials are added 0.5000 g to 1.0000 g \pm 0.0005 g of asphalt in 0.1 to 0.2 gram increments, respectively. Toluene (LC-grade) is added to each vial in 1.000 mL \pm 0.005 mL aliquots and the vials are capped and the asphalt sample is allowed to dissolve. Figure 1 depicts the apparatus that has been assembled to perform the automated procedure. The vials containing asphalt solutions are loaded into a reaction vessel maintained at 25°C (77°F) with a temperature controlled water bath and stirred for ten minutes. The temperature controlled solutions are circulated through a 0.1 mm flow cell housed within a UV-visible spectrophotometer using 0.16 cm (1/16") ID viton tubing and a metering pump. The titrant, either iso-octane (LC-grade) or n-heptane (LC-grade) which is also maintained at a constant temperature of 25°C \pm 0.1°C (77°F) is introduced into the vial through 0.055 cm (0.022") ID viton tubing with a second metering pump set at a fixed flow rate in the range of 0.300 mL/min to 0.500 mL/min. The change in the percent transmittance at an absorbance wavelength of 740 nm is plotted as a function of titrant flow rate and chart speed on a strip chart recorder. Figure 2 shows a typical

series of titration curves for asphalt AAD-1, one of the Strategic Highway Research Project (SHRP) core asphalts. The volume of titrant added is related to the distance from the start of a curve, when titrant is first introduced, to the apex of the peak (the onset of flocculation), L_p . Heithaus parameters are calculated using values of V_T that are calculated as:

$$V_T = \left(\frac{L_p}{v_c} \right) v_T \quad (6)$$

where L_p is the distance to the apex of the peak measured in centimeters, v_c is the chart recorder speed in cm/min and v_T is the titrant flow rate in mL/min.

Crossblend mixtures were prepared by mixing an arbitrary amount of maltenes from either asphalt with a specified amount of asphaltenes at the natural abundance level of the asphaltenes in either asphalt, resulting in eight different mixtures. Four of the mixtures have either AAF-1 or AAG-1 asphaltenes, four have either AAF-1 or AAG-1 maltenes, and four are mixed at either the AAF-1 or AAG-1 natural abundance level. Sample mixtures were labeled in terms of maltene type (M), asphaltene type (A), and asphaltene natural abundance level (L). Asphaltene and maltene fractions were mixed in round bottom flasks along with dichloromethane, used to dissolve and disperse the materials. Crossblend mixtures were dried using heat and vacuum distillation.

RESULTS AND DISCUSSION

Repeatability in the automated method is influenced by several variables. These are as follows: **Sample concentrations:** It was observed that with concentrations less than 0.50 g/mL, that plots of flocculation ratio (FR) versus concentration (C) deviated from linearity. This is assumed to be related to the pathlength of the flow cell; 0.10 mm used in this work. And when solutions greater in concentration than 1.1 g/mL are tested, several hours are required for complete sample dissolution, increasing the likelihood for sample oxidation due to prolonged exposure to the aerated solvent. This left only a narrow range of solution concentrations with which to work with, thus placing a greater emphasis on accuracy in other variables relevant to the procedure, such as accurate sample weights, consistency in titrant flow rate, and consistency in circulation flow rate. **Temperature:** It was found to be necessary to control both solution temperature and the titrant temperature as well to within 0.1°C. Fluctuations in lab temperature were also found to affect repeatability in data, making recording lab temperature standard practice. **Titrant flow rate and flow rate consistency:** It was found that in order to achieve an accuracy of approximately 0.05 in the value of P that the flow rate had to be steady to within 0.005 mL/min over a 20 minute period or longer, and that the flow rate had to be below 0.500 mL/min with the sample sizes that were being used. **Circulation flow rate:** It is necessary to control flow rate because solution viscosities increase with increasing concentrations. It was found that the circulation flow rate needs to be as fast as possible, at minimum the circulation flow rate needed to run at a rate of 10 mL/min and to vary no less than 0.5 mL/min when more concentrated solutions were tested. **Stirring rate, for mixture homogeneity and temperature control:** The stirring rate needed to be fast enough to adequately mix the solution, but not so fast as to heat the solution. **Titrating solvent (iso-octane in place of n-heptane):** It was found that certain waxy asphalts (AAC-1 and AAM-1 for example) were difficult or impossible to test using n-heptane as the titrating solvent. When iso-octane, which has a lower solubility parameter ($\delta = 6.90$) than n-heptane ($\delta = 7.46$), was used in place of n-heptane, all SHRP core asphalts could be tested. For non-waxy asphalts, n-heptane is a suitable titrant.

It was determined from a statistical analysis that poor repeatability in the classical procedure was due to systematic error. Figure 3 shows that a correlation, $R^2 = 0.94$ may be drawn between the weight percent of n-heptane asphaltenes for six SHRP core asphalts when plotted versus sample standard deviations in P parameters obtained using the classical procedure. It was surmised that removal of sample from solution for the purpose of performing the spot test to detect the onset of flocculation was the source of operator error in the classical procedure. With more compatible asphalts this error would be more pronounced because, for compatible asphalts (relatively low levels of asphaltenes) more titrant is required to promote the onset of flocculation and the spot testing is performed more often throughout the titration.

Table 1 shows Heithaus parameter and sample standard deviation data collected by three different operators using the automated procedure titrated with iso-octane, and sample standard deviation data collected by a single operator using the classical procedure, titrated with n-heptane for SHRP core asphalt AAD-1. It is seen from Table 1 that data gathered on this asphalt by three different operators using the automated procedure is almost as repeatable as data gathered by a single operator using the classical procedure. It has been found that compatibility data gathered for asphalts having

higher concentrations of asphaltenes (incompatible) generally give repeatable results using the classical procedure.

The problem that arises in the classical procedure lies in gathering repeatable data for asphalts having lower concentrations of asphaltenes (compatible). Thus, Table 1 shows a notable improvement in data gathered for a compatible SHRP core asphalt; AAM-1, in terms of sample standard deviation values of Heithaus compatibility parameters using both procedures.

Figure 4 depicts P-values for seven SHRP core asphalts using the classical procedure and titrated with n-heptane, plotted versus P-values using the automated procedure and titrated with iso-octane as being consistent with one another. It is not to be expected that the Heithaus parameters obtained by either method will be identical when different titrants are used. Similar plots using p_a and p_o values for the same seven SHRP core asphalts were not in as good agreement. According to Branthaver et al.⁸ asphaltenes precipitated from asphalts using iso-octane were found to have different physical properties than asphaltenes precipitated using n-heptane. This raised the question of what p_a and p_o values actually measure. Two hypotheses were formulated. First, p_a and p_o values are representative of the types of asphaltenes and maltenes, respectively found in a particular asphalt; or alternatively, p_a and p_o values are representative of the amount of asphaltenes present in an asphalt.

To verify which hypothesis was correct, asphaltene/maltene crossblend mixtures were prepared from asphaltene and maltene fractions separated from a compatible asphalt (AAG-1) and a somewhat less compatible asphalt (AAF-1). Table 2 shows compatibility data collected on eight AAG-1/AAF-1 crossblend mixtures that were titrated with n-heptane using the automated procedure. Results in Table 2 show p_a -values being more closely related to natural asphaltene abundance levels (L) and P-values also somewhat related to natural asphaltene abundance levels. Table 2 also shows p_o values being weakly related to asphaltene type (A), but not asphaltene concentration (C).

CONCLUSION

The application of an automated procedure to test asphalt compatibility appears feasible. Results show the automated procedure to be less operator dependent and more rapid than the classical procedure. Several variables relating to the repeatability of the automated procedure have been isolated, among them; sample concentrations, temperature, circulation, stirring and titrant flow rates, and titrating solvent. Heithaus P parameters measured for seven SHRP core asphalts using both automated and classical procedures show the data to be consistent from one procedure to the other. Asphaltene/maltene crossblend mixtures prepared using SHRP core asphalts AAG-1 and AAF-1 were tested using the automated procedure. Results for crossblend mixtures show that measured values of p_a relate more closely to an asphalt's asphaltene concentration, whereas, p_o values appear to be influenced by asphaltene type.

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Table 1. Comparison of the repeatability in data obtained using either the automated or classical procedure.

Asphalt, procedure, operator:		Heithaus parameters		
		P _a	P _o	P
AAD-1, automated:	Operator-1	0.688	0.682	2.18
	Operator-2	0.686	0.731	2.32
	Operator-3	0.701	0.637	2.13
	Average	0.691	0.683	2.21
	Std. Dev.	0.008	0.047	0.10
AAD-1, classical, single operator:	Average	0.61	1.33	3.43
	Std. Dev.	0.01	0.02	0.04
AAM-1, automated, single operator:	Average	0.907	0.66	7.08
	Std. Dev.	0.006	0.10	0.59
AAM-1, classical, single operator:	Average	0.89	1.26	12.19
	Std. Dev.	0.03	0.04	2.59

Table 2. Heithaus parameters of AAG-1/AAF-1 asphaltene-maltene crossblend mixtures.

Crossblend Mixture Design M A L *	Heithaus parameters		
	P _a	P _o	P
G F F	0.67	1.11	3.35
F F F	0.67	1.03	3.09
G F G	0.76	1.07	4.48
F F G	0.64	2.72	7.59
G G G	0.77	1.37	6.02
F G F	0.66	1.45	4.28
G G F	0.68	1.43	4.41
F G G	0.77	1.04	4.46

*M: maltene type, A: asphaltene type, L: natural abundance level of asphaltenes in asphalt listed.

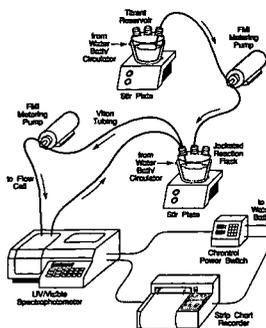


Figure 1. Apparatus used in automated Heithaus procedure.

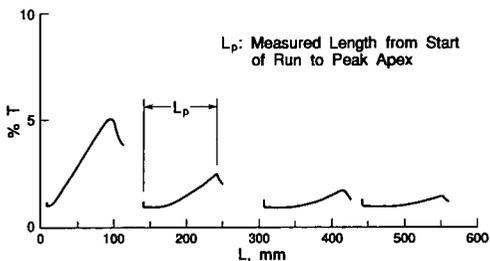


Figure 2. Flocculation peaks of one SHRP core asphalt; AAD-1.

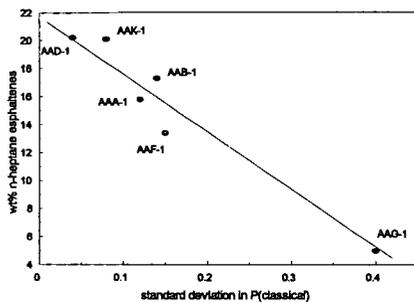


Figure 3. The relationship between asphaltene concentration and sample standard deviations in average values of the parameter.

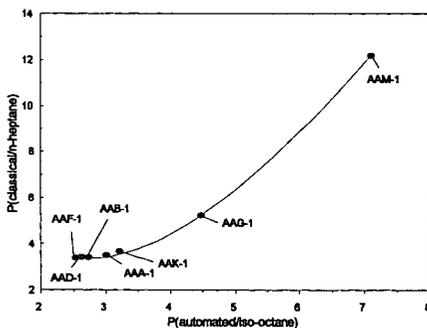


Figure 4. Relationship between Heithaus P parameters obtained using the automated procedure and the classical procedure.