

Compatibilities of Strategic Highway Research Program Asphalts

J. F. BRANTHAVER, J. C. PETERSEN, J. J. DUVALL, AND
P. M. HARNSBERGER

The so-called colloidal model of asphalt structure views asphalts as dispersions of relatively aromatic, polar, associating molecules in a less aromatic, less polar solvent phase. The extent to which solvent phases disperse associating species, therefore, should determine many fundamental properties of asphalts, and measurements of states of dispersion should allow for prediction of important properties. States of dispersion, or compatibility, of eight virgin asphalts studied in the Strategic Highway Research Program were measured by several methods. These methods were the Heithaus titration method, measurements of asphaltene yields by precipitation with *n*-heptane followed by iso-octane, measurements of relative viscosities (viscosity of asphalt divided by viscosity of maltenes) at different temperatures, and determination of sulfur content. All these methods served to identify two asphalts as being fundamentally much more compatible than the other six. Among the other six less well dispersed, less compatible asphalts, the methods did not serve to differentiate one from another in the same way. For the eight asphalts studied, determining the sulfur content or measuring *n*-heptane asphaltene yields appeared to be equally good as indicators of compatibility as the more complicated methods. Absolute viscosities of asphalts do not correlate with asphalt compatibilities, as is well known. However, relative viscosities determined by dividing asphalt viscosities by maltene viscosities (the maltenes are considered to be the solvent phase) appear to be good indicators of asphalt compatibilities.

One of the primary objectives of the Strategic Highway Research Program (SHRP) is to develop performance-related tests that are based on fundamental properties. According to one widely accepted model (the so-called colloidal model), asphalts are associations of polar, aromatic molecules that are dispersed in a nonpolar solvent phase. This model predicts that the effectiveness of the solvent phase in dispersing the associated phase should strongly influence many of the physical properties of asphalts. The state of dispersion, or compatibility, of an asphalt therefore should be an important fundamental property (1).

A method that is commonly used to determine the compatibility of asphalts is the Heithaus titration method (2,3). This method involves dissolving a specified amount of asphalt in varying amounts of toluene and measuring the amounts of *n*-heptane required to cause flocculation in each of the solutions. From these data, parameters are calculated that estimate the state of peptization of an asphalt (P), the peptizability of its asphaltenes (P_a), and the peptizing power of its maltenes (P_o). Most asphalts contain substantial amounts of

asphaltenes, which are solids that precipitate when asphalts are mixed with several volumes of alkanes with low molecular weight. The residual materials remaining after separation of asphaltenes and solvent removal are referred to as maltenes. In the Heithaus method, asphaltenes are identified as the equivalent of the asphalt-dispersed phase, and maltenes are identified as the equivalent of the solvent phase.

Asphaltene yields resulting from mixing asphalts with large volumes of alkanes are a function of the structure of the precipitating solvent (4). For example, with *n*-heptane, asphaltene yields are lower than for *n*-pentane. The heptane asphaltenes also are more aromatic and contain more of the heteroatoms N, O, and S than the pentane asphaltenes. This is because the solubility parameter (δ) of *n*-pentane ($\delta = 7.18$) is somewhat less than that of *n*-heptane ($\delta = 7.46$). The branched hydrocarbon iso-octane (2,2,4 trimethylpentane) has a solubility parameter of 6.90, which is substantially lower than that of *n*-pentane. When this solvent is used to precipitate asphaltenes from an asphalt, yields are high and the asphaltenes are relatively aliphatic and contain smaller concentrations of heteroatoms.

The asphaltene fraction, however prepared, is known to have a large influence on the viscosity of an asphalt. Deasphalted asphalts (maltenes) are much less viscous than their parent asphalts measured under identical conditions. However, correlations between viscosity and asphaltene concentrations of different asphalts are not good (5). Two asphalts having nearly identical viscosities can have significantly different asphaltene concentrations.

The lack of a good correlation between asphaltene concentrations and viscosities for different asphalts is probably due to compositional differences among asphalts, which may be reflected in differences in compatibilities of asphalt components. A particular asphalt might consist of highly viscous maltenes but have a relatively small amount of polar molecules comprising its dispersed asphaltenes. Another asphalt might consist of much less viscous maltenes but contain more polar materials in its dispersed asphaltenes. These two asphalts might have similar viscosities (although other rheological properties would differ) but would be expected to have quite different asphaltene contents if *n*-heptane or *n*-pentane were used as precipitating solvent (6). The first asphalt would be designated as a well-dispersed system, and the second would be designated as a poorly dispersed system.

When asphaltenes are precipitated by *n*-heptane, polar molecules are partitioned between the insoluble asphaltenes and soluble maltenes. Most of these polar molecules are assumed

Western Research Institute, Box 3395, University Station, Laramie, Wyo. 82071.

to be viscosity builders. Their solubility in *n*-heptane is governed by the types of functional groups they contain, by their molecular weights, and to a lesser degree by subtle differences in their molecular structures. Most, if not all, the asphaltenes precipitated by *n*-heptane presumably form part of the asphalt-dispersed phase. Molecules precipitated by *n*-heptane are highly polar molecules of high and low molecular weight, and less polar molecules of higher molecular weight. Some relatively polar molecules will remain in the maltene fraction when asphaltenes are precipitated from an asphalt by *n*-heptane. Because petroleum consists of compound types that often exist as homologous series that range over many carbon numbers, some components of asphaltenes may resemble those in maltenes fairly closely. Individual compounds may be found in both asphaltenes and maltenes in different concentrations if the compounds have measurable solubilities in *n*-heptane. Therefore, this solvent will not remove all polar molecules from asphalts.

The branched hydrocarbon iso-octane is a much poorer solvent for polar molecules than *n*-heptane. When heptane maltenes are mixed with iso-octane, more asphaltenes precipitate. Almost all polar viscosity-building molecules not precipitated by *n*-heptane should be precipitated in the iso-octane asphaltenes. This precipitate should include the remainder of the asphalt-dispersed phase and some of the "resins" that are critical factors in effecting compatibility of the asphalt-dispersed phase with the asphalt-solvent phase. The iso-octane maltenes should show some similarity to the asphalt-solvent phase if the colloidal model of asphalt structure is valid.

Relative amounts of *n*-heptane and iso-octane asphaltenes should vary from one asphalt to another. Some asphalts contain large amounts of highly polar molecules. Others are characterized by relatively aromatic solvent phases, which retain polar molecules in solution even when treated with large volumes of *n*-heptane. Asphalts with large amounts of highly polar molecules and aliphatic solvent phases may be considered to be poorly dispersed systems, or relatively incompatible systems. Such asphalts should be characterized by large yields of asphaltenes when treated with *n*-heptane, and the heptane maltenes should not yield comparatively large amounts of asphaltenes when treated with iso-octane. Asphalts with small amounts of polar molecules engaging in associations, and which have aromatic solvent phases, should be characterized by small yields of *n*-heptane asphaltenes. Their *n*-heptane maltenes should yield relatively large amounts of asphaltenes when treated with iso-octane. These asphalts are well dispersed, or compatible. Thus, the yield of asphaltenes obtained by mixing an asphalt with several volumes of *n*-heptane should be an indicator of the compatibility of a system. The relative amounts of the two types of asphaltenes should be a better indicator of compatibility than yields of *n*-heptane alone. If this is so, relative yields of both kinds of asphaltenes for an asphalt should correspond to some degree with results derived from Heithaus titrations.

Relative viscosities also should be measures of compatibilities of asphalt systems. In order to calculate relative viscosities, it is arbitrarily assumed that *n*-heptane maltenes resemble asphalt-solvent phases fairly closely (although not as closely as iso-octane maltenes). Thus, relative viscosities discussed later are quotients of the asphalt absolute viscosities divided by maltene absolute viscosities measured under identical con-

ditions. High relative viscosity values should be characteristic of poorly dispersed systems, and low relative viscosity values should be characteristic of well-dispersed systems. When relative viscosities are plotted versus temperature, curves that have relatively flat slopes should be observed for well-dispersed systems (assuming temperature is the abscissa). Poorly dispersed systems should exhibit steep relative-viscosity-temperature curves. This is because heat improves the compatibility of an incompatible system more than a compatible one.

Elemental composition of an asphalt is not necessarily an indicator of compatibility. Asphalts with differing elemental concentrations of elements may have similar compatibilities. However, those asphalts having large heteroatom (N, O, S) contents usually are observed to have large yields of asphaltenes, and asphalts relatively deficient in heteroatoms usually are characterized by low asphaltene yields.

EXPERIMENTAL METHODS

The asphalts studied were the eight core asphalts selected by SHRP for intensive study. Asphalt AAA-1 is 150/200 penetration grade and is a distillation residue. Asphalt AAB-1 is AC-10 grade and is a distillation residue. Asphalt AAC-1 is AC-8 grade and is a distillation residue. Asphalts AAD-1 and AAG-1 are AR-4000 grade and are distillation residues. Asphalts AAF-1 and AAM-1 are AC-20 grade and are solvent deasphalted asphalts. Asphalt AAK-1 is AC-30 grade and is a distillation residue.

Asphaltenes were prepared by mixing 40 volumes *n*-heptane (EM Sciences, Omni-Solv, glass distilled) for each gram of asphalt in Erlenmeyer flasks of appropriate sizes. After standing 16 hr with occasional swirling, the contents of the flasks were poured onto sintered glass funnels (M porosity) resting on suction flasks. Asphaltenes were washed several times with *n*-heptane, and washings were combined with the filtrate. The filtrate then was transferred to a round-bottom flask, and the solvent was removed on a rotary evaporator using heat and reduced pressure. The residual *n*-heptane maltenes were checked for solvent levels of below 0.1 percent by gas chromatographic-simulated distillation. Asphaltenes adhering to the Erlenmeyer flask were removed and combined with the filter cake. The asphaltenes were pulverized, dried, and weighed. They were stored under an inert gas atmosphere for future study.

Portions of the *n*-heptane maltenes were mixed with 40 volumes of iso-octane (J. T. Baker, high-performance liquid chromatography-grade) in Erlenmeyer flasks of appropriate sizes. After 16 hr, during which the flasks were occasionally swirled, the contents of the flasks were filtered and processed as for the *n*-heptane-treated asphalt samples above. Iso-octane maltenes and asphaltenes are the products of this treatment. The precipitated iso-octane asphaltenes are black, friable solids, as are the *n*-heptane asphaltenes.

Asphaltene compatibility indexes (ACIs) were obtained by dividing the weight percent of iso-octane asphaltenes (based on amount of total asphalt) by the sum of the weight percents of *n*-heptane and iso-octane (based on amount of total asphalt) asphaltenes and multiplying the quotient by 10. Thus, for AAA-1 the calculation is $[3.4/(15.8 + 3.4)] \times 10 = 1.77$. Actual yields of iso-octane yields from *n*-heptane maltenes

are corrected to yields based on total asphalt by multiplication by *n*-heptane maltene weight fractions. Thus the actual yield of iso-octane asphaltene from *n*-heptane maltenes of asphalt AAA-1 was 4.04 weight percent. This number was multiplied by $(100 - 15.8)/100 = 0.842$, which is the weight fraction of *n*-heptane maltenes in AAA-1, to obtain the iso-octane asphaltene yield of 3.4 weight percent based on total asphalt.

Heithaus titrations were performed using a method developed by Heithaus (2) and modified by Kiggundu et al. (7) and in our laboratories. In this improved procedure, four 1.0 g samples of the test asphalt were weighed into 125 mL Erlenmeyer flasks. To the four flasks were added amounts of 1.0, 2.0, 4.0, or 6.0 mL toluene (Burdick and Jackson, redistilled prior to use). Dissolution of the asphalt in toluene may take several hours at ambient temperatures. Use of heat is not advised due to potential loss of solvent. After dissolution was complete, a stirring bar was added to each flask, and the flasks were immersed in a water bath maintained at 25°C (77°F) for 30 min. The flasks then were titrated with 1.0 mL aliquots of *n*-heptane (Phillips Petroleum Company, 99 percent, redistilled over calcium hydride before use). After each addition of *n*-heptane, the contents of the flask were stirred 5 min on a magnetic stirrer. Flocculation was determined by transferring a drop of the solution to a filter paper with a glass rod. The development of two rings on the filter paper is indicative of flocculation. Otherwise, only one ring is observed. For replicate determinations of an asphalt, all but 1 mL of the amount of *n*-heptane required for flocculation may be added at once, followed by addition of 0.1 mL increments. For some asphalts, flocculation points could not be determined for the samples mixed with 1.0 mL toluene. In these cases, 1.0 g asphalt was dissolved in 8.0 mL toluene, so that the four flasks contained 2.0, 4.0, 6.0, and 8.0 mL toluene, respectively.

If and when asphaltene flocculation was observed, Heithaus parameters were calculated as follows:

$$\text{Flocculation Ratio: FR} = \frac{V_T}{V_T + V_H}$$

$$\text{Dilution Ratio: } X = \frac{V_T + V_H}{W_A}$$

where

V_T = volume of toluene in flask,

V_H = volume of *n*-heptane required for flocculation, and

W_A = weight of asphalt in flask (1.00 ± 0.05 g).

These calculations resulted in four values of FR and four values of X . A graph in which FR is plotted versus $1/X$ was prepared. A straight line was drawn through the data points and extrapolated to both axes. The intercept with the ordinate is FR_{\max} . The intercept with the abscissa is $1/X_{\min}$, from which X_{\min} is calculated. These two values were used to calculate P_a , P_o , and P as follows:

Peptizability of asphaltene, $P_a = 1 - FR_{\max}$

Peptizing power of maltenes, $P_o = FR_{\max}(X_{\min} + 1)$

State of peptization of asphalt, $P = P_o/(1 - P_a) = X_{\min} + 1$

Viscosity measurements were performed on a Rheometrics mechanical spectrometer. Asphalts and maltenes measured were flooded with argon and placed in an oven at 110°C (230°F) for 1 hr and 10 min. After the samples were removed from the oven, rheological measurements were made within 40 to 60 hr. If this "annealing" step is not performed, viscosity determinations will be erratic. Relative viscosities were calculated by dividing absolute viscosities of asphalts by absolute viscosities of their *n*-heptane maltenes determined at the same temperature and rate of shear.

Molecular weight determinations were performed by vapor phase osmometry in toluene or pyridine at 60°C (140°F).

Elemental analyses were performed by the analytical services division of Western Research Institute using standard methods.

RESULTS

SHRP has designated eight asphalts for intensive study, and these asphalts are referred to as "core asphalts." Code designations for these core asphalts and some of their chemical and physical properties are reported in Table 1. The relative aromaticities of the eight asphalts are not greatly different, as indicated by their H/C ratios, but heteroatom contents vary considerably. Sulfur concentrations range from 1.2 percent for AAM-1 to 6.9 percent for AAD-1. The high nitrogen content of AAG-1 is noteworthy. Number-average molecular weight (MW) values are similar for seven of the asphalts, but the MW of AAM-1 is significantly larger.

Seven of the core asphalts were titrated by the method of Heithaus (2) to obtain the parameters P , P_a , and P_o . The parameter P is a measure of the state of dispersion of the asphalt as a whole. A large P value indicates a well-dispersed or highly peptized system. The parameter P_a measures peptizability of asphaltene. As P_a increases, asphaltene should be more readily solvated. The parameter P_o measures the solvent power of maltenes, here identified with the dispersing phase. A large P_o value indicates that the dispersing phase is a good solvent. The values of each of these three parameters for each of seven core asphalts obtained in duplicate measurements are reported in Table 2. Reproducible data could not be obtained for AAC-1, probably because of the waxy nature of this asphalt.

Asphalts AAM-1 and AAG-1 stand out from the other five for at least two of the three Heithaus parameters. Their average values of P indicate that they are much better peptized, or well-dispersed, systems than the other five asphalts. The asphaltene of AAG-1 and AAM-1 are also more readily dispersed, as shown by high average P_a values. The values for P_o exhibit substantial variances for most of the asphalts, so firm conclusions about maltene solvent powers are not readily drawn. The average P_o values range from 1.13 (Asphalt AAA-1) to 1.33 (Asphalt AAD-1) and thus indicate that AAD-1 maltenes have the best solvation powers of all the asphalts tested. Yet, from the P value for AAD-1, it would appear that AAD-1 is not a well-dispersed system. This may be due to the high asphaltene content and low asphaltene peptizability (P_a) of AAD-1, discussed later. The Heithaus parameters P_a and P_o measure inherent properties of asphaltene and maltenes and do not take into account relative quantities of these materials in an asphalt.

TABLE 1 ELEMENTAL ANALYSES AND MOLECULAR WEIGHTS OF EIGHT CORE ASPHALTS

Asphalt and Asphalt Grade	Element, wt%					H/C	MW (Toluene)
	C	H	N	O	S		
AAA-1, 150/200 pen	84.2	10.5	0.50	0.60	5.50	1.48	790
AAB-1, AC-10	82.3	10.6	0.60	0.80	4.70	1.54	840
AAC-1, AC-8	86.5	11.3	0.70	0.90	1.90	1.56	870
AAD-1, AR-4000	81.4	10.8	0.80	0.90	6.90	1.58	700
AAF-1 ¹ , AC-20	84.5	10.4	0.50	1.10	3.50	1.47	840
AAG-1, AR-4000	85.6	10.5	1.10	1.10	1.30	1.46	710
AAK-1, AC-30	80.7	10.2	0.70	0.80	6.40	1.51	860
AAM-1 ¹ , AC-20	86.7	11.4	0.60	0.50	1.20	1.57	1300

¹Asphalts AAF-1 and AAM-1 were obtained by solvent deasphalting. The other six asphalts are distillation residua.

TABLE 2 HEITHAUS PARAMETERS FOR SEVEN ASPHALTS

Asphalt	Run Number	P	P _a	P _o	Asphalt	Run Number	P	P _a	P _o
AAA-1	1	3.29	0.69	1.02	AAG-1	1	5.30	0.80	1.06
	2	3.50	0.68	1.12		2	5.80	0.80	1.16
	3	3.56	0.68	1.14		3	5.50	0.80	1.10
	4	3.26	0.65	1.14		4	4.65	0.74	1.21
	5	<u>3.42</u>	<u>0.64</u>	<u>1.23</u>		5	<u>4.96</u>	<u>0.74</u>	<u>1.29</u>
	Avg.	3.41	0.67	1.13		Avg.	5.24	0.78	1.16
AAB-1	1	3.30	0.67	1.09	AAK-1	1	3.73	0.67	1.23
	2	3.65	0.66	1.24		2	3.79	0.67	1.24
	3	3.62	0.63	1.34		3	3.56	0.68	1.14
	4	<u>3.49</u>	<u>0.63</u>	<u>1.29</u>		4	3.60	0.65	1.26
	Avg.	3.51	0.65	1.24		5	<u>3.66</u>	<u>0.65</u>	<u>1.28</u>
AAD-1	1	3.42	0.62	1.30	AAM-1	Avg.	3.67	0.66	1.25
	2	3.50	0.62	1.33		1	15.87	0.92	1.27
	3	3.47	0.62	1.32		2	14.87	0.92	1.19
	4	3.40	0.60	1.36		3	14.62	0.92	1.17
	5	<u>3.38</u>	<u>0.60</u>	<u>1.35</u>		4	10.50	0.86	1.47
	Avg.	3.43	0.61	1.33		5	10.57	0.86	1.48
AAF-1	1	3.55	0.62	1.35		6	9.58	0.88	1.15
	2	3.39	0.62	1.29		7	<u>9.33</u>	<u>0.88</u>	<u>1.12</u>
	3	3.53	0.62	1.34		Avg.	12.19	0.89	1.26
	4	3.27	0.63	1.21					
	5	<u>3.17</u>	<u>0.64</u>	<u>1.14</u>					
	Avg.	3.38	0.63	1.27					

Asphaltenes were prepared from all eight core asphalts by precipitation with n-heptane. After solvent was removed from each of the maltene fractions, iso-octane was mixed with the maltenes to precipitate more asphaltenes. Elemental analyses and MWs of the two types of asphaltenes are reported in Table 3 for one series of runs for each of the core asphalts.

For each of the core asphalts, the n-heptane asphaltenes are more aromatic and of higher MW than the iso-octane asphaltenes, as would be expected. Asphaltene aromaticities and MWs vary considerably among asphalts. Asphaltene MWs do not appear to relate to compatibility as measured by Heit-haus parameters *P*, because the asphaltenes from AAM-1

TABLE 3 ELEMENTAL ANALYSES AND MOLECULAR WEIGHT DETERMINATIONS FOR ASPHALTENES OF CORE ASPHALTS

Asphalt	Asphaltene Type	Element, wt%					H/C	Molecular Weight	
		C	H	N	O	S		Toluene	Pyridine
AAA-1	heptane	80.6	7.8	1.2	1.5	8.5	1.15	8,000	5,800
	iso-octane	80.8	8.3	0.9	1.8	8.2	1.22	4,500	3,700
AAB-1	heptane	84.9	7.4	1.4	1.2	5.2	1.04	6,500	4,600
	iso-octane	83.9	7.7	1.1	1.5	5.9	1.09	4,500	3,400
AAC-1	heptane	86.4	7.6	1.4	1.1	3.4	1.05	5,000	4,400
	iso-octane	86.6	8.1	1.2	1.2	3.1	1.11	2,800	2,800
AAD-1	heptane	79.9	8.1	1.8	1.9	8.8	1.21	7,400	4,600
	iso-octane	79.8	8.8	1.4	2.0	8.1	1.31	3,500	2,600
AAF-1	heptane	84.1	7.1	1.0	1.6	6.4	1.01	4,500	3,600
	iso-octane	84.9	8.0	0.8	1.6	5.4	1.12	2,600	2,300
AAG-1	heptane	82.7	7.8	2.2	2.9	1.5	1.12	5,500	3,100
	iso-octane	84.4	8.2	2.2	2.4	1.2	1.16	3,000	2,100
AAK-1	heptane	80.9	7.9	1.7	1.5	6.7	1.16	7,900	Insol
	iso-octane	81.0	8.4	1.3	1.6	7.6	1.24	4,500	3,900
AAM-1	heptane	83.9	7.7	1.1	1.4	2.4	1.13	10,000	Insol
	iso-octane	86.9	8.6	1.0	1.1	1.9	1.18	7,200	insol

are of high MW and those of AAG-1 are of low MW. These two asphalts supposedly are the most highly peptized systems, on the basis of the Heithaus data. For most of the asphaltenes, MW determinations in pyridine are much lower than MW determinations in toluene, particularly for the n-heptane asphaltenes. This is because pyridine has a higher solubility parameter ($\delta = 10.3$) than toluene ($\delta = 8.9$) and more effectively breaks up asphaltene associations. For Asphalts AAC-1 and AAF-1, iso-octane asphaltenes have nearly identical MWs determined both in pyridine and in toluene. These asphaltenes are therefore weakly associating, and the MW values of 2,300 to 2,800 probably represent monomeric or dimeric molecular species.

For some of the iso-octane asphaltenes, sulfur and oxygen concentrations are greater than in the corresponding n-heptane asphaltenes. Nitrogen concentrations in the n-heptane asphaltenes are greater than or equal to the iso-octane asphaltenes for all core asphalts.

Table 4 reports yields of duplicate runs of asphaltene precipitations by n-heptane and iso-octane for each of the eight core asphalts. With the exception of Asphalts AAG-1 and AAM-1, yields of n-heptane asphaltenes are much greater than yields of iso-octane asphaltenes. For these two asphalts, total asphaltene yields are much lower than total asphaltene yields of the other six core asphalts. The ACI data shown in Table 4 will be discussed later.

Inspection of Tables 2 and 4 shows that low yields of n-heptane asphaltenes and relatively high Heithaus P values distinguish Asphalts AAG-1 and AAM-1 from the other core asphalts. Assuming the Heithaus method to be a meaningful measure of asphalt compatibility, then a high P value should

correlate with a low yield of asphaltenes when an asphalt is treated with n-heptane. For the other five asphalts for which Heithaus P values were obtained, that parameter does not readily distinguish one from another. Based on Heithaus P values, AAF-1 is the most poorly dispersed system and AAK-1 the most well dispersed of the five. The P values, however, do not vary greatly, ranging from 3.38 to 3.67. The n-heptane asphaltene concentrations of the five asphalts vary considerably, from 13.4 percent to 20.2 percent. Therefore, among asphalts with similar Heithaus P values, n-heptane asphaltene concentration may not accurately measure state of dispersion if it is assumed that the Heithaus P values are correct indicators of peptization. Alternatively, it is possible that the Heithaus P value is not a good indicator of relative compatibilities among incompatible asphalts. The other two Heithaus parameters of the five asphalts having similar P values cannot be used to demonstrate that any one differs from the other four in a meaningful way because either the P_a values are similar or there is too much error in the P_o measurement.

Table 5 reports viscosities of each of the core asphalts obtained on a mechanical spectrometer at 25°C (77°F) and 60°C (140°F), and 1.0 radian/sec rate of shear. Viscosities at 60°C (140°F) vary considerably from one asphalt to another, and viscosities at 25°C (77°F) vary greatly when measured with the mechanical spectrometer. This is to be expected, as the asphalts vary in grade from AC-8 to AC-30. Asphalts AAB-1, AAF-1, and AAG-1 have high temperature coefficients of viscosity, whereas AAK-1 has a lesser variance of viscosity with temperature. Comparison of the data in Table 5 with data in Table 2 and 4 shows that there is little correlation with viscosity at 25°C (77°F) or 60°C (140°F) with either the Heit-

TABLE 4 ASPHALTENE YIELDS AND ACIs OF CORE ASPHALTS

Asphalt	Operator (Initials)	Heptane Asphaltenes (HA), wt%	Iso-octane Asphaltenes (IA), wt%	ACI, $\left(\frac{IA}{HA}\right) \times 10$
AAA-1	MS	15.1	3.8	1.77
	MC	16.6	3.0	
	Average	15.8	3.4	
AAB-1	MC	17.1	2.2	1.04
	MC	17.6	1.8	
	Average	17.3	2.0	
AAC-1	MC	9.8	3.1	2.40
AAD-1	MC	19.7	3.6	1.44
	SP	20.8	3.3	
	Average	20.2	3.4	
AAF-1	MC	13.2	2.7	1.88
	JW	13.7	3.5	
	Average	13.4	3.1	
AAG-1	MS	4.9	3.4	3.97
	MC	5.1	3.3	
	Average	5.0	3.3	
AAK-1	MS	19.2	3.4	1.22
	MC	20.9	2.3	
	Average	20.1	2.8	
AAM-1	MC	3.4	4.6	5.93
	SP	4.1	6.2	
	Average	3.7	5.4	

haus parameter P or n-heptane asphaltene yields. If the Heit-haus parameter P or n-heptane asphaltene yields measure the compatibility of a system, then the absolute viscosity of an asphalt is not a direct function of compatibility. This is why correlations between asphaltene concentrations and viscosities among various asphalts have not been observed. Many years ago, Traxler (8) observed that the absolute viscosities of asphalts do not necessarily correlate with other rheological properties of asphalts. He noted that well-dispersed asphalt systems exhibited little non-Newtonian behavior or thixotropy but were often characterized by high absolute values of viscosity and high temperature coefficients of viscosities. Poorly dispersed systems exhibit considerable non-Newtonian behavior (or complex flow, as defined by Traxler), lesser temperature coefficients of viscosities, but they may be of high or low absolute viscosities. Parameters that measure compatibilities should correlate with complex flow and variation in viscosity with temperature, but not necessarily with absolute viscosity. Absolute viscosity would appear to be a function of asphalt preparation, because it is a made-to-order property.

Table 6 reports viscosities of n-heptane maltenes of eight asphalts at 25°C (77°F) and 60°C (140°F). The high viscosities

TABLE 5 VISCOSITIES OF EIGHT ASPHALTS AT 25°C AND 60°C, 1.0 RADIAN/SEC

Asphalt	Temperature, °C	Viscosity, poises
AAA-1	25	275,400
	60	1,245
AAB-1	25	1,125,000
	60	1,507
AAC-1	25	945,400
	60	1,194
AAD-1	25	405,700
	60	1,644
AAF-1	25	3,078,000
	60	2,893
AAG-1	25	3,540,000
	60	2,998
AAK-1	25	1,077,000
	60	4,703
AAM-1	25	3,180,000
	60	4,539

TABLE 6 VISCOSITIES OF MALTENE¹ FRACTIONS OF EIGHT ASPHALTS AT 25°C AND 60°C, 1.0 RADIAN/SEC

Asphalt	Temperature, °C	Viscosity, poises
AAA-1	25	8,040
	60	77
AAB-1	25	30,200
	60	85
AAC-1	25	105,000
	60	248
AAD-1	25	3,290
	60	36
AAF-1	25	250,000
	60	334
AAG-1	25	1,143,000
	60	1,316
AAK-1	25	16,200
	60	123
AAM-1	25	1,018,000
	60	1,394

¹ Maltenes obtained by precipitation of asphaltenes with n-heptane.

of asphalts have low asphaltene contents (AAM-1, AAG-1, and AAF-1) because of the high viscosities of their maltenes. Maltene viscosities appear to correlate with Heit-haus P values and inversely with n-heptane asphaltene yields. The maltenes having relatively high viscosities may be part of systems so well dispersed that many viscosity-building polar components

are not precipitated by n-heptane. It may be possible that these materials are precipitated by iso-octane. Inspection of Table 4 shows that iso-octane asphaltene yields derived from n-heptane maltenes are relatively low for all eight asphalts and range from 2.0 percent to 5.4 percent. Yields of n-heptane asphaltenes are greater than 5.4 percent for all asphalts except Asphalt AAM-1, for which the n-heptane asphaltene yield is only 3.7 percent. This is the only asphalt having a greater amount of iso-octane asphaltenes than n-heptane asphaltenes. For Asphalt AAG-1, the yield of n-heptane asphaltenes is comparable to the yield of iso-octane asphaltenes from the n-heptane maltenes. These are the two asphalts whose n-heptane maltene viscosities are highest. Therefore, those asphalts having low yields of n-heptane asphaltenes may yield relatively large amounts of asphaltenes when their n-heptane maltenes are treated with iso-octane, and presumably some viscosity-building materials would be included in these iso-octane asphaltenes. Thus an asphalt having a low n-heptane asphaltene content may be higher in absolute viscosity than an asphalt having a large amount of n-heptane asphaltenes. Asphalts having relatively large amounts of iso-octane asphaltenes must be well-dispersed systems, and asphalts having relatively small amounts of iso-octane asphaltenes must be poorly dispersed systems for which n-heptane is sufficient to remove almost all polar viscosity-building materials. On the basis of these criteria, Asphalt AAM-1 is the most well dispersed of the eight asphalts, followed closely by AAG-1. Asphalt AAB-1 is the least well dispersed system, followed closely by AAK-1 (see ACI values in Table 4 and the discussion of them).

It is likely that iso-octane does not remove all viscosity-building materials from asphalts but does so to varying degrees among the asphalts. Viscosity data on iso-octane maltenes have yet to be measured. These maltenes should approximate real solvent phases of asphalts in their rheological properties more so than n-heptane maltenes. It is likely that some asphalts have solvent phases that are relatively more aromatic and more viscous than others.

A parameter designated as the ACI was calculated for each of the core asphalts (Table 4). This factor is 10 times the quotient of the average iso-octane asphaltene yield divided by the total average asphaltene yield (sum of n-heptane and iso-octane asphaltene yields). This parameter measures the relative amounts of the two asphaltene types in an asphalt. Intuitively, asphalts with high ACI values should be well-dispersed systems and asphalts with low ACI values should be poorly dispersed systems. Comparison with the Heithaus titration data (Table 2) shows that the ACI values correspond to the Heithaus parameters P reasonably well. Both parameters identify Asphalts AAM-1 and AAG-1 as being fundamentally different from the other asphalts tested. Both of these asphalts are much better dispersed systems than the five other asphalts for which Heithaus parameters and ACI values were obtained. Among the five poorly dispersed asphalts, the Heithaus method indicates that AAF-1 is the most poorly dispersed system; the ACI index indicates that AAB-1 is the most poorly dispersed. The differences in Heithaus parameters P among Asphalts AAA-1, AAB-1, AAD-1, AAF-1, and AAK-1 are not great. The ACI parameter provides a measure of the state of dispersion of AAC-1, for which P cannot be measured reproducibly, indicating that it is intermediate between AAG-1, AAM-1, and the other five asphalts. A plot

of Heithaus P values versus ACI values for seven asphalts is shown in Figure 1.

Except for AAB-1 and AAD-1, ACI values correlate with n-heptane asphaltene yields in assessing asphalt dispersibilities for the eight asphalts measured. A large number of asphalts are observed to have asphaltene contents in the 18 to 22 percent range when n-heptane is used as precipitating solvent. The states of dispersion of such asphalts are not high, but they vary significantly. It is hoped that the combination of iso-octane asphaltene yields with n-heptane asphaltene yields into ACI values can provide more information about asphalt compatibility for the large number of asphalts of this type than n-heptane asphaltene yields alone. Determination of asphaltene yields by n-heptane is sufficient to identify outliers such as Asphalts AAG-1 and AAM-1, which are well-dispersed systems.

If absolute viscosities of asphalts do not correlate with indexes of compatibility but maltene viscosities do, then relative viscosity values for the asphalts may be related to compatibility. To calculate relative viscosities, n-heptane maltenes are assumed to approximate the asphalt solvent phase. The absolute viscosity of an asphalt then is divided by the absolute viscosity of its n-heptane maltenes at the same temperature and shear rate (Table 7) to obtain relative viscosities. Relative viscosities of asphalts may be compared at a given temperature, and the change in relative viscosities with temperature may be measured to provide information about asphalt compatibilities. As an illustrative example from polymer science, for solutions of polymers in good solvents (compatible systems), relative viscosity versus temperature curves are flat and nearly parallel the abscissa. Polymers dissolved in poor solvents (incompatible systems) are characterized by steep relative viscosity versus temperature curves (9).

Examination of Table 7 shows that the values of the relative viscosities of Asphalts AAM-1, AAG-1, AAC-1, and AAF-1 are low at 25°C (77°F) and 60°C (140°F) and are not greatly different at the two temperatures. For the other four asphalts, relative viscosity values are high at 25°C (77°F) but much lower at 60°C (140°F). In these asphalts, heating results in considerable breakup of molecular associations as a result of a great improvement in the solvent power of the dispersing

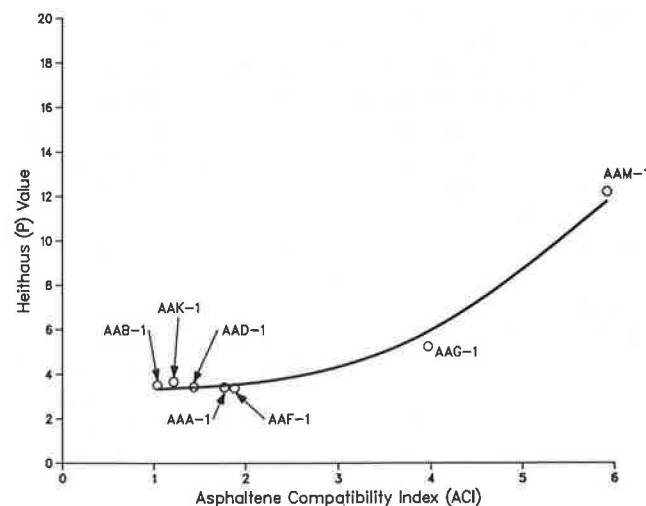


FIGURE 1 State of peptization of core asphalts versus ACI.

TABLE 7 RELATIVE VISCOSITIES¹ OF ASPHALTS AT TWO TEMPERATURES, 1.0 RADIAN/SEC

ASPHALT	RELATIVE VISCOSITY	
	25 °C	60 °C
AAA-1	34.2	16.2
AAB-1	37.3	17.3
AAC-1	9.0	4.8
AAD-1	123.3	45.7
AAF-1	12.3	8.7
AAG-1	3.1	2.3
AAK-1	66.5	38.2
AAM-1	3.1	3.3

¹ Relative viscosities are calculated by dividing absolute viscosities of each asphalt at a given temperature by the absolute viscosity of its n-heptane maltene.

phase. For the four incompatible, or poorly dispersed asphalts, asphalt viscosities decrease with increasing temperature relatively more than maltene viscosities. It would appear that relative viscosity measurements of asphalts provide a direct indication of compatibility. On the basis of this criterion, the asphalts may be ranked in order of relative increasing compatibility as AAD-1 < AAK-1 < AAB-1 < AAA-1 < AAF-1 < AAC-1 < AAG-1 < AAM-1. This ranking holds at either temperature of measurement (Table 7). Relative viscosities of the asphalts are plotted versus three other measures of compatibilities in Figures 2, 3, and 4. The correlation between n-heptane asphaltene content and relative viscosity (Figure 2) is better than the correlations of ACI values or sulfur contents with relative viscosity (Figures 3 and 4).

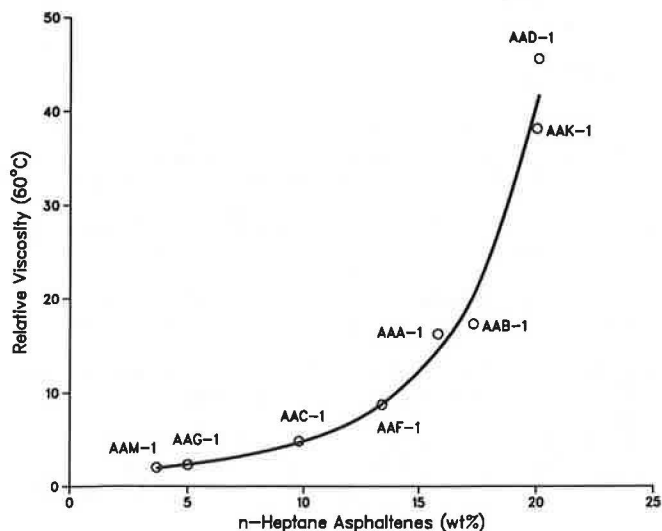


FIGURE 2 Relative viscosity of core asphalts as related to n-heptane asphaltenes.

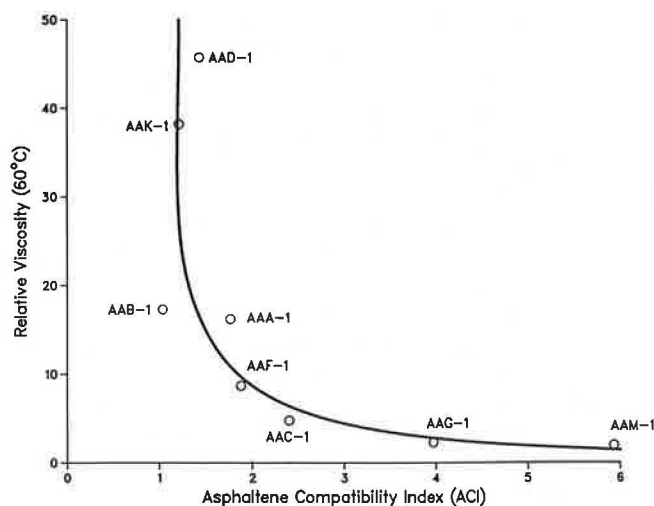


FIGURE 3 Relative viscosity of core asphalts versus ACI.

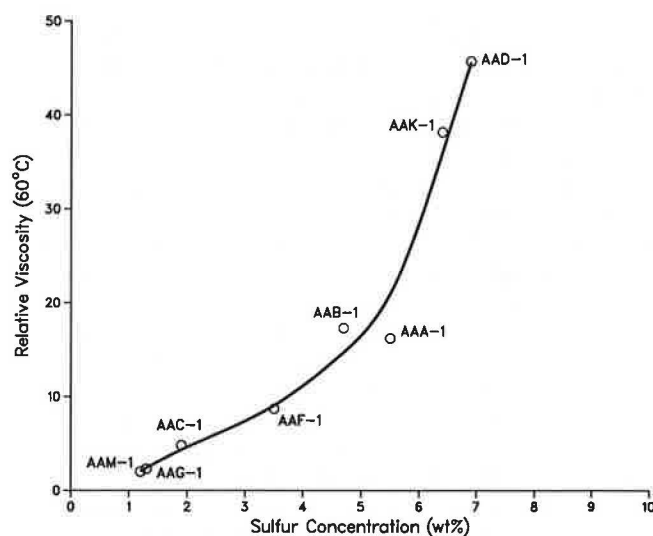


FIGURE 4 Relative viscosity of core asphalts as related to sulfur content.

SUMMARY AND CONCLUSIONS

Seven asphalts were titrated by the Heithaus method to obtain parameters that are presumed to measure the compatibility, or state of dispersion, of the asphalts. By this method, two asphalts were identified as particularly well dispersed systems. Five other asphalts were identified as being relatively poorly dispersed systems and did not show significant differences among their Heithaus parameters from one asphalt to another. One asphalt that was part of this study could not be titrated by the Heithaus method because of excessive wax content.

Asphaltene contents using n-heptane as precipitating solvent were determined for the eight study asphalts. The maltenes resulting from this process were treated with iso-octane, causing additional precipitation of asphaltene. Viscosities of the asphalts and the maltenes derived from n-heptane treatment were measured at 25°C (77°F) and 60°C (140°F). Ele-

mental analyses and molecular weights were obtained for the asphalts and both the n-heptane and iso-octane asphaltenes. Asphaltene contents of the asphalts as defined by n-heptane precipitation correlate inversely, but poorly with the Heithaus parameter (P). The two asphalts identified as well-dispersed systems by the Heithaus method are characterized by low n-heptane asphaltene yields. The n-heptane asphaltene yields of the other asphalts were much higher and varied more than their Heithaus parameters. For unaged asphalts, measuring n-heptane asphaltene yields may be as accurate as Heithaus titration in assessing states of dispersion.

Absolute viscosities of the eight asphalts at two temperatures did not correlate with either Heithaus parameters (P) or n-heptane asphaltene yields. Absolute viscosity of an asphalt therefore is not a direct function of state of dispersion, as pointed out by earlier workers. This is because the maltene fractions of some of the asphalts are highly viscous and those of others are not. If relative viscosities are calculated for each asphalt by dividing absolute viscosities of asphalts by absolute viscosities of their n-heptane maltenes measured under identical conditions, then these relative viscosities correlate with n-heptane asphaltene yields and less well with Heithaus P values. Asphalts having low n-heptane asphaltene yields have maltenes with high viscosities, and vice versa.

Iso-octane precipitates additional amounts of asphaltenes from n-heptane maltenes. Yields of these iso-octane asphaltenes vary somewhat among the eight asphalts examined. For two of the asphalts, yields were comparable to those obtained by n-heptane, but they were less for the other six. The two asphalts characterized by the largest iso-octane asphaltene concentrations were the two with the highest Heithaus P values. An index incorporating both yields of n-heptane and iso-octane asphaltenes was developed that measured compatibility somewhat differently than the Heithaus method or that measured n-heptane asphaltene yields alone. This index was designated as the ACI. It is similar to one developed earlier in these laboratories in which asphaltene yields were determined by mixing each of these two solvents with whole asphalts. The two asphalts with the highest Heithaus P values also had the highest ACI values. Two other asphalts with moderate yields of n-heptane asphaltenes also had fairly high ACI values. Heithaus P values could not be obtained for one of these. The ACI index ranks the remaining four asphalts slightly different with regard to compatibility than n-heptane asphaltene yields alone.

Iso-octane asphaltenes are lower in molecular weight than n-heptane asphaltenes from the same asphalts. They are also less aromatic, but not necessarily lower in heteroatom content.

Sulfur concentrations of asphalts correlate well with n-heptane asphaltene yields, as is well known. Sulfur concentrations of asphalts also correlate inversely with Heithaus P values and with ACI values. Asphalts containing small amounts of sulfur tend to be well-dispersed systems, and asphalts containing large amounts of sulfur are poorly dispersed systems. This is to be expected, as sulfur contents of asphalts are a measure of the ages of their parent crudes. Mature crudes should contain less sulfur compounds because of degradation of reactive components over time.

When the several methods used to evaluate the states of dispersion, or compatibilities, of eight unaged asphalts were compared, all methods readily distinguish two asphalts as being

much more highly dispersed than the others. Heithaus P parameters do not serve to distinguish the other asphalts studied from one another very well. Yields of n-heptane asphaltenes, which may be as good a criterion as any for rapidly estimating compatibilities of unaged asphalts, correlate inversely with relative viscosities for all eight asphalts. Sulfur contents and asphaltene compatibility indexes rank the asphalts slightly different with respect to compatibility than do n-heptane asphaltene yields and relative viscosities. These last four named indicators all identify four asphalts as being poorly dispersed systems and two of the other four asphalts as being well-dispersed systems. The remaining two asphalts are of an intermediate nature. The evaluation of these methods will be extended to blends and to aged asphalts, in which sulfur concentrations can hardly be expected to serve as indicators of compatibility, and n-heptane asphaltene yields may not prove to be as useful as for virgin unblended asphalts. More accurate measurements of asphalt compatibilities may be compared with physical property data to determine which physical properties are functions of states of dispersion.

ACKNOWLEDGMENTS

The work reported herein has been conducted as a part of a SHRP project being conducted by the Western Research Institute, Laramie, Wyoming, in cooperation with the Pennsylvania Transportation Institute, Texas Transportation Institute, and SRI International. Raymond E. Robertson is the principal investigator. The support and encouragement of Edward Harrigan and Jack Youtcheff is gratefully acknowledged. Heithaus titrations were performed by J. M. Wolf and M. V. Aldrich. Asphaltenes and maltenes were prepared by M. W. Catalfomo, S. C. Preece, and M. A. Scott. Viscosity determinations were performed by H. Plancher and F. A. Reid. Molecular weight determinations were performed by G. W. Gardner and B. W. Lowry. Elemental analyses were performed by the analytical services division of Western Research Institute. The manuscript was prepared by M. Knadler and J. Greaser. The authors are grateful to R. E. Robertson for a thoughtful review.

REFERENCES

1. J. C. Petersen. Chemical Composition of Asphalt as Related to Asphalt Durability: State of the Art. In *Transportation Research Record 999*, TRB, National Research Council, Washington, D.C., 1984, pp. 13–30.
2. J. J. Heithaus. Measurement of Significance of Asphaltene Precipitation. *Preprints, Division of Petroleum Chemistry, American Chemical Society*, Vol. 5, 1960, pp. A23–A37.
3. J. J. Heithaus. Measurement and Significance of Asphaltene Precipitation. *Journal of the Institute of Petroleum*, Vol. 48, 1962, pp. 45–53.
4. R. B. Girdler. Constitutions of Asphaltenes and Related Studies. *Proc., Association of Asphalt Paving Technologists*, Vol. 34, 1965, pp. 45–79.
5. H. Plancher, E. L. Green, and J. C. Petersen. Reduction of Oxidative Hardening of Asphalts by Treatment with Hydrated Lime—A Mechanistic Study. *Proc., Association of Asphalt Paving Technologists*, Vol. 45, 1976, pp. 1–24.
6. K. H. Altgelt and O. M. Harle. The Effect of Asphaltenes on Asphalt Viscosity. *Industrial and Engineering Chemistry, Product Research and Development*, Vol. 14, 1975, pp. 240–247.

7. B. M. Kiggundu, B. Nusser-Humphrey, and D. M. Zallen. *Recycling Agent Selection and Tentative Specification*. USAF Report ESL-TR-84-47. 1984.
8. R. N. Traxler. *Asphalt, Its Composition, Properties, and Uses*. Reinhold, New York, N.Y., 1961.
9. E. T. Severs. *Rheology of Polymers*. Reinhold, New York, N.Y., 1962.

The contents of this paper reflect the views of the authors, who are solely responsible for the facts and accuracy of the data presented. The

contents do not necessarily reflect the official view or policies of SHRP or its sponsors. The results reported here are not necessarily in agreement with the results of other SHRP research activities. They are reported to stimulate review and discussion within the research community. This paper does not constitute a standard, specification, or regulation. Mention of specific brands of materials does not imply endorsement by SHRP or the Western Research Institute.

Publication of this paper sponsored by Committee on Characteristics of Bituminous Materials.