

Thermodynamic Behavior and Physicochemical Analysis of Eight SHRP Bitumens

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In order to determine criteria for the characterization of bitumens from physical data and to analyze their thermodynamic behavior during thermal cycles, a homogeneous series of eight bitumens provided by the National Research Council as part of the Strategic Highway Research Program was studied. Thermodynamic properties (e.g., transformation temperatures, crystallized fractions, enthalpy changes, expansion and compressibility coefficients, pressure-temperature state diagrams) were studied using four complementary methods of analysis: differential scanning calorimetry, thermomicroscopy, thermobarometry, and thermodilatometry. The chemical compositions were defined by gel permeation chromatography, high-performance liquid chromatography, and synchronous excitation-emission ultraviolet fluorescence. Evidence of modification of physical properties, especially during thermal cycles, compared with the proportions of the different chemical components is shown and discussed.

All laboratories that attempt to understand the complex nature of bitumens with a view to improving their application in road techniques are interested in the work of the Strategic Highway Research Program (SHRP), since this large American program has a similar goal (1). The authors have therefore analyzed the same bitumens with emphasis on additional data provided either by an apparatus not previously applied to these bitumens or by an alternative interpretation.

The aim of this study of the physical and physicochemical properties and behavior of bitumens is to show that at customary temperatures (-10°C to $+50^{\circ}\text{C}$), melting is accompanied by complex transformations that entail accompanying variations of rheological properties. However, the desired properties of coated materials are primarily mechanical (resistance to rutting, cracking, loss of binder, and thermal and mechanical fatigue); the rheological properties of bitumens, whether aged or not (and of binders more generally), will therefore play a basic role in the field behavior of coated

materials. Any research aimed at a better understanding of the relation between physicochemical characteristics and rheological properties of bitumens is then of interest. In addition to the traditional characterization tests [penetrability at various temperatures, ring-and-ball softening temperature (RBT), artificial aging in the rolling thin-film oven test (RTFOT)], measurements of thermodynamic magnitudes by differential scanning calorimetry (DSC) and thermobarometry and measurements of behavior under small strains (complex modulus) were carried out. The object of this paper is to sum up the results.

COLLOIDAL STRUCTURE OF BITUMENS (2)

Derived from the distillation of crude oil, road bitumens are complex organic media both in their large number of constituents and in the nature of the associations that make them macroscopically homogeneous and viscous materials. When fractionation by selective precipitation is attempted, it is found that *n*-alkanes can be used to isolate a family of insoluble products called asphaltenes, the soluble part being called maltenes. This fractionation has been known for a long time and has enabled many researchers to perform numerous analyses of composition and structure. It was not until the work by Yen in 1961 on asphaltenes alone (3) that better definitions of the terms *micelle* and *cluster* became available. According to Yen, the molecules of asphaltenes are in an associated state either in the form of micelles (elementary entities of a few lamellae of molecules) or in the form of packets of micelles called clusters (these lamellae and clusters are held together by forces of the hydrogen-bond type, induced or permanent dipoles, and pi-pi bonding). Given this description and the incompatibility of this chemical family with *n*-alkanes, it is easier to understand that, according to their chemical composition, the maltenes more or less completely scatter these micelles and clusters. Diagrams of this colloidal structure may be found in earlier papers (4,5). To arrive at a better understanding of the rheological behavior, this model has the advantage over other models in surpassing the molecular scale and incorporating the microscopic scale. In effect, any rheological study assumes that the matter is continuous, and thus the molecular scale cannot be used (6). The discontinuity of the molecular distribution (in property and in size) as sug-

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gested in this study is not an obstacle to the rheological approach; rather it is favorable to the interpretation of the observed differences in linear behavior.

TRADITIONAL TESTS

The results of the traditional tests by the ELF laboratory and the Laboratoire Central des Ponts et Chaussées (LCPC) and those of the SHRP data base are given in Table 1. They suggest the following remarks:

1. If an attempt is made, before artificial aging, to group the bitumens by grade according to the French standards (7), it is found that (a) AAF1, AAG1, AAK1, and AAM1 belong to the 60/70 class (commonly used for hot mixes); (b) AAB1 and AAC1 belong to the 80/100 class (commonly used for hot mixes, surface dressing, or emulsions); (c) AAD1 belongs to the 100/140 class (commonly used for surface dressing or emulsions); and (d) AAA1 belongs to the 180/220 class (commonly used for surface dressing or emulsions). After RTFOT it is found that they lose, on average, one class.

2. The temperature sensitivities are very different and their values depend on the method of calculation, which suggests that the hypothesis of Pfeiffer and Van Doormaal (penetrability of 800 0.1 mm at the softening temperature) (8) is not verified.

3. The arrangement according to temperature sensitivity (penetration index PI) by class is the following:

LCPC PI: AAF1 \cong AAG1 < AAM1 < AAK1 and AAC1 < AAB1

Pfeiffer PI: AAG1 < AAF1 < AAM1 < AAK1 and AAC1 \cong AAB1

The arrangement is the same before and after artificial aging: bitumen AAG1 is the most sensitive and bitumen AAK1 the least sensitive to temperature.

4. The indices of colloidal instability for bitumens AAG1 and AAM1 are low (0.07 and 0.09), which places these bitumens among the stable bitumens of the sol type; it will be noted that they have little asphaltenes and that AAM1 is very rich in aromatics for the class; bitumens AAF1 and AAK1, with a higher index (0.17 and 0.24), are closer to French bitumens.

SIMULATED DISTILLATION

Simulated distillation by gas chromatography is based on the principle of elution of compounds in the order of their boiling points (9). This has been strictly verified only for nonpolar compounds and for stationary phases that are also nonpolar. The experimental conditions and the method of calculation of the boiling points have been given in previous papers (10,11).

One of the important characteristics of bitumen is durability, which can be defined as the ability to retain the initial rheological properties under the conditions of service. Volatility, measured by loss of mass, is a criterion found in the standards of most countries, but the methods used for this measurement are not very discriminating and so not very useful. Simulated distillation, a more precise technique, gives a fingerprint of the light compounds and allows their quantitative evaluation. Applied to evaluate the volatility of

TABLE 1 Usual Technological Characteristics Before and After RTFOT

		AAA1	AAB1	AAC1	AAD1	AAF1	AAG1	AAK1	AAM1		
Before	RBT °C	*	44.6	47.4	46.5	40.9	50.2	48.5	50.0	49.5	
		**	40.1	45.2	45.0	44.2	49.2	48.0	50.1	48.1	
		***	44.4	47.8	42.7	47.8	50.0	48.9	49.4	51.6	
	Pen. 25 °C	*	153	88	96	127	54	49	70	65	
		**	155	90	102	137	54	55	65	63	
		***	160	98	133	135	55	53	70	64	
	RTFOT	Penetration Index LCPC	*	-0.71	-0.81	-1.70	-0.71	-1.39	-1.10	-0.38	-0.81
			**	-1.10	-1.00	-1.80	-1.80	-2.20	-3.3	-1.30	-1.20
		Penetration Index Pfeiffer	*	+0.59	-0.45	-0.45	-1.46	-0.97	-1.62	+0.37	-0.70
			**	-1.10	-1.00	-0.70	-0.10	-1.20	-1.50	-0.50	-1.10
***			0.70	0.00	-0.62	1.13	-0.97	-1.34	-0.53	-0.20	
% Asphaltenes		*	14.2	13.3	7.3	18.5	10.3	3.7	17.3	3.1	
		**	11.5	13.7	12.1	15.0	9.3	3.3	12.0	2.7	
		Colloidal Instability Index	*	0.24	0.22	0.16	0.29	0.17	0.09	0.24	0.07
**			0.19	0.28	0.30	0.25	0.19	0.09	0.19	0.11	
After		RBT °C	*	47.0	52.7	51.5	52.0	54.5	51.6	56.5	54.5
	**		46.6	51.4	50.3	52.4	54.0	50.6	57.0	51.0	
	Pen. 25 °C		*	87	56	56	66	33	36	42	46
		**	80	56	54	60	29	35	40	42	
		RTFOT ^a	Penetration Index LCPC	*	-0.53	-0.13	-0.55	+0.07	-0.43	-1.58	+0.31
	**			-	-	-	-	-	-	-	-
	Penetration Index Pfeiffer		*	-0.60	-0.27	-0.56	+0.02	-1.04	-1.51	-0.10	-0.33
		**	-0.90	-0.60	-0.90	-0.20	-1.40	-1.80	-0.10	-1.30	

(*LCPC - **ELF - ***SHRP)

^aASTM D 2872

TABLE 2 Content of Volatile Matter

	Percentage of matter distilling up to 480°C	Percentage of matter distilling up to 540°C
AAA1	13.6 (1 to 12)	26.0 (8 to 29)
AAB1	4.9 (1 to 8)	13.4 (5 to 28)
AAC1	1.8 (1 to 8)	5.7 (5 to 28)
AAD1	19.1	29.9
AAF1	4.0 (1 to 5)	11.8 (7 to 18)
AAG1	7.0 (1 to 5)	18.7 (7 to 18)
AAK1	14.3 (1 to 5)	23.0 (7 to 18)
AAM1	1.2 (1 to 5)	2.3 (7 to 18)

(volatilities of French bitumens in 1991 are in parentheses)

the eight SHRP bitumens, this technique gave the results for the bitumens shown in Table 2, three of which are shown in Figure 1.

Of the bitumens AAF1, AAG1, AAK1, and AAM1, which belong to the same class (60/70 for hot mixes), only AAK1 has a volatile matter content in the upper limits. The volatile matter content of the others lies approximately within the range for their class. Bitumen AAM1 is remarkable for its low volatile matter content.

At excessively high volatilities, one can wonder about the long-term evolution of the rheology of these bitumens. Furthermore it is necessary to report that bitumens rich in volatile matter cause (blue) fumes to be emitted in coating plants, thereby harming the environment. Unfortunately, the maximum values of volatility have not yet been specified.

GEL PERMEATION CHROMATOGRAPHY (GPC)

Brûlé has shown that GPC, under special conditions (high concentration and rapid flow rate), can approach the structural character of bitumens. Thus, the presence of a population of very large molecules or of highly associated entities of smaller sizes (12) is detected on the chromatogram by the presence of a peak called the "interaction peak" at the exclusion volume of the column. GPC is therefore an analytical

technique that can reveal the existence of more or less intense intermolecular interactions.

The usual GPC data are given in detail in the publications of Jennings et al. (13,14) and Brenthaver et al. (15); only the key facts concerning "ultrafast" GPC are discussed here. Three types of structures can be distinguished according to whether the bitumen consists of one (AAC1, AAG1, AAF1), two (AAB1, AAM1), or three (AAA1, AAD1, AAK1) molecular modes. Each of these populations that elutes under a peak is quantified by a convolution program that also serves to determine the mean molecular mass corresponding to each entity. Simultaneous detection at 350 and 410 nm and by differential refractometry reveals the following:

- Presence of a population of low molecular mass (AAD1, AAK1) responding at 410 nm,
- Shift in the maximum elution volume between the ultraviolet at 350 nm and differential refractometry (AAA1, AAD1, AAK1) whenever an interaction peak is observed and not otherwise (Figure 2), and
- Bitumen AAM1 consisting of large molecules with respect to the mass usually detected in the other asphalts.

Note that UV detection (340 and 410 nm) is not sufficient to obtain the true mass distribution. UV detection gives information only about condensed aromatic compounds. If it is

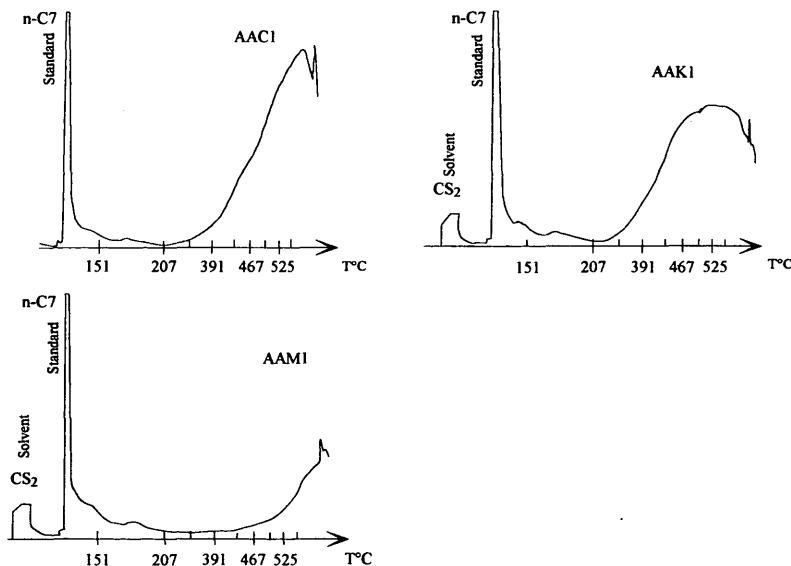


FIGURE 1 Chromatograms of simulated distillation for three asphalts.

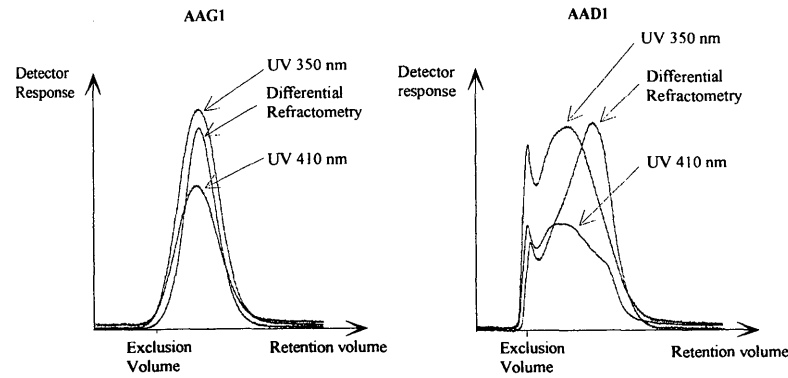


FIGURE 2 Ultrafast GPC chromatograms for three SHRP asphalts.

assumed that the response coefficients of UV detection are located on a unique curve for different asphalts, as Brûlé has shown (16), this detection can be used to compare the variation in mass distribution of the aromatic molecules for different road asphalts. Artificial aging is reflected in an increase in the population of the largest molecules.

SYNCHRONOUS EXCITATION-EMISSION FLUORESCENCE

Synchronous excitation emission (17) (SEE), developed in cooperation with research on the evolution of the structure of coal (18), has recently been applied to road bitumens (19). The phenomenon of UV fluorescence deals with the electron excitation of molecules that have π -electrons. Aromatic molecules are therefore analyzed.

SEE spectra are produced by recording the fluorescence intensity of a mixture while the excitation and emission wavelengths are made to vary at the same time with a constant offset. SEE is a useful tool for the analysis of aromatic substances because

- It responds to the properties characteristic of both absorption and emission, and
- Each molecule is represented by a single peak, which considerably simplifies the spectrum in the case of complex mixtures.

The position of the fluorescence peaks depends on the number of condensed aromatic rings. Substances listed in the literature were used to determine the zones with one ring, two rings, three to four rings, and five rings (20). All the bitumens analyzed have practically the same spectral fingerprint between 250 and 600 nm, and their maximum intensity is at 398 nm (Figure 3).

The differences in intensity are due in part to asphaltene, present in quantities that vary from one bitumen to another. Asphaltene has a net extinction effect. An increase in the asphaltene content induces a decrease in the fluorescence intensity.

The aging of the binder during coating, placement, or on site is reflected in modification of the rheological properties that can be linked, among other things, to the appearance of chemical functions (carboxylic, ketonic, anhydric, hydroxylic)

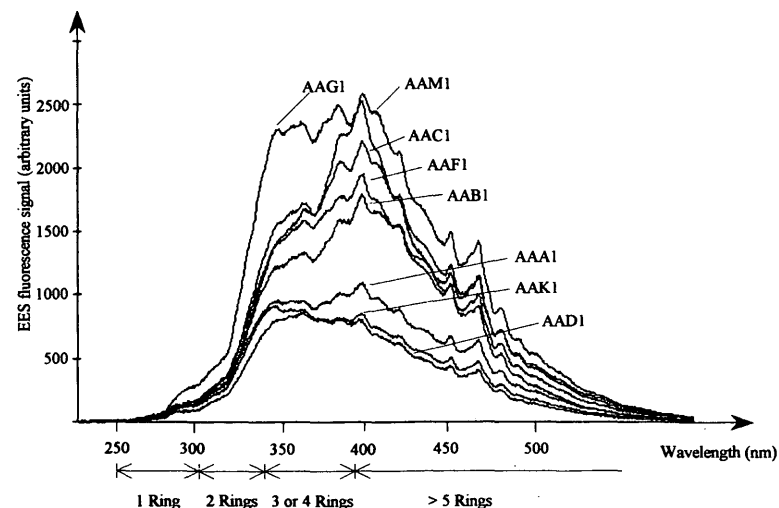


FIGURE 3 Fluorescence spectra of eight SHRP asphalts.

together with intermolecular rearrangements. SEE fluorescence spectroscopy serves to monitor the evolution of the aromatic compounds during the aging of a bitumen.

The eight SHRP bitumens analyzed constitute a broad range of polyaromatic substances and so allowed the determination of a few general tendencies (Figure 3):

- The ratio of the relative intensities of five rings to two rings most sharply discriminates among the eight bitumens;
- AAM1 is distinguished by a high fluorescence of three to four rings with respect to two rings;
- AAG1 has the smallest proportion of highly condensed rings;
- Aging mainly affects the highly condensed polyaromatics;
- Extinction of fluorescence after aging of bitumen AAM1 is highly marked; it has been noted that it consists mainly of three to four aromatic rings; and
- Bitumen AAG1, rich in small rings, aged more homogeneously over the whole spectrum.

This technique coupled with GPC shows that the fluorescence of the interaction peak is practically zero; the second population has a spectrum that corresponds to the fluorescence of compounds with three to four and five polyaromatic rings; and the third population, which corresponds to the smaller molecules, fluoresces in the zone of only slightly condensed aromatic rings. The spectral response of the fluorescence is therefore in agreement with the distribution of molecular sizes.

Analyzed by size-exclusion chromatography using UV detection (at 340 nm), the largest molecules are highly aromatic materials but their fluorescence is weak compared with the usual fluorescence intensities of aromatic ring models. This alteration of the fluorescence is consistent with the presence of molecular interactions. This interpretation agrees with Branthaver (15).

The diversity of the sampling also made it possible to find, for these bitumens, a relation between the colloidal instability

index and the maximum intensity of fluorescence at 398 nm. This linear relation ($r = 0.84$), which seems to be independent of the origin and production of the bitumen, should be extended to other samples.

COMPLEX MODULUS

The rheological behavior of road bitumens was characterized on the basis of tests using small sinusoidal strains at frequencies between 5 and 250 Hz. This complex modulus test was performed at low temperatures (-30°C to $+30^{\circ}\text{C}$) in the tension-compression mode on cylindrical specimens (diameter = 0.9 cm; thickness = 1.8 cm) of bitumen and at temperatures between $+20^{\circ}\text{C}$ and $+60^{\circ}\text{C}$ in the annular shear mode, with the bitumen trapped between a piston and its cylinder. The characteristics of the equipment used (vicoanalyser METRAVIB) have been described by Duperray and Leblanc (21).

The results are given in Figure 4, which shows the isotherms of the moduli and a representation of the master curve in Black's space (22); this representation has the advantage of avoiding any smoothing of the experimental points and highlights any nonequivalence of time and temperature.

As in the study of GPC, the work of Anderson and others has led to a detailed analysis of the eight core bitumens (23). A mathematical model has been proposed for the complex shear modulus G^* and for the phase angle δ . Therefore all the results of this study are not given here, only new results and interpretations.

The model used for quantitative interpretation is that proposed by Jongepier and Kuilman (24). It allows a Gaussian distribution on the logarithmic scale of relaxation times τ ; the relaxation spectrum $H(\tau)$ is log normal. The dynamic sensitivity depends on R in Anderson's mathematical model and on σ in Jongepier and Kuilman's model. The relaxation time, defined by the intersection of the vitreous and viscous asymp-

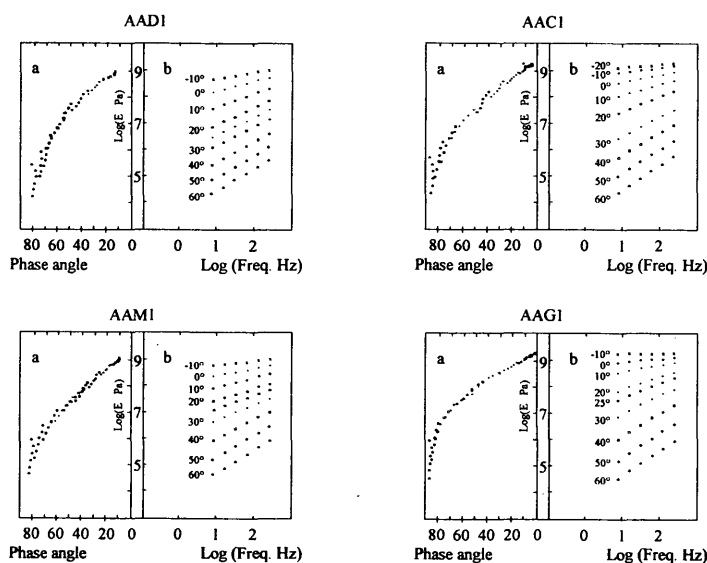


FIGURE 4 Complex modulus of four asphalts: (a) Black's representations, (b) isothermal curves.

totes, corresponds to $1/\omega_0$ and τ_0 , respectively. The results are given in Table 3.

Examination of the modulus curves of the eight bitumens in Black's space shows the following characteristics:

1. The experimental points are not always on a single curve; the isotherm forms "waves" in Black's space. Repeatability of the phase angles is determined within 1.2° or less. Unicity (i.e., a single curve in Black's space) is not satisfied by bitumens AAM1 and AAD1; poorly satisfied by AAA1, AAB1, and AAC1; and rather well satisfied by AAF1, AAK1, and AAG1. However, when the master curve is constructed by recording the modulus versus the reduced frequency, a well-defined curve can be observed for the real part of the modulus, a less well-defined curve for the imaginary part, and a (more or less) badly defined curve for the phase angle. The non-unicity means that the microscopic edifice of the bitumen has a nonequivalent response when studied in terms of frequency (time) or temperature; this generally occurs when transitions (vitreous or otherwise) are possible in the frequency and temperature range used. This microscopic edifice is linked to the existence of clusters in interaction, to the presence of molten crystallizable matter (such as paraffins), or to both. Parameters and τ_m of the model are in this case calculated from the nearest envelope curve.

2. If one compares the curves of bitumens AAG1 and AAK1, the phase angle of bitumen AAG1 increases much faster with the logarithm of the modulus, and its isotherms have steeper slopes and are more closely spaced. This implies a larger dynamic and temperature sensitivity for AAG1 than for AAK1.

3. The curves in Black's space of bitumens AAD1 and AAK1 are practically the same; the isotherms, while offset, have similar slopes, and so the dynamic sensitivities of the two bitumens are not very different. The unicity of AAD1 is mediocre, even though this bitumen is less viscous than AAK1.

4. Bitumen AAM1, poor in asphaltene and having a standard deviation σ smaller than that of AAK1, has a rheological behavior typical of a bitumen regarded as "paraffinic."

5. The low value of the complex modulus of AAM1 for a phase angle of 45° is noted.

TABLE 3 Main Composition and Rheological Characteristics

	I.C.	% Asphaltene	σ^a	$\log \tau_m^b$ (50 °C)
AAM1	0.07	3.1	3.75 *	-8.6 *
AAG1	0.09	3.7	3.30	-8.0
AAC1	0.16	7.3	3.30	-8.2
AAF1	0.17	10.3	3.40	-8.9
AAB1	0.22	13.3	3.80 *	-8.9 *
AAA1	0.24	14.2	4.00 *	-9.4 *
AAK1	0.24	17.3	4.10	-9.1
AAD1	0.29	18.5	4.10 *	-9.5 *

*Mean value of envelope curve

^a Standard deviation in Joneprier and Kuilman's model

^b Median relaxation time in Joneprier and Kuilman's model

$$\tau_0 = \tau_m e^{-\frac{\sigma^2}{2}}$$

THERMOBAROMETRY AND THERMODILATOMICROSCOPY

Principle of Thermobarometric Analysis

Thermobarometric analysis (25) consists of recording the pressure variations versus temperature of a sample enclosed in a rigid housing. Any first-order transition will be detected by a sudden large increase of pressure reflecting the existence of discontinuities for the entropy (ΔS) and the molar volume (ΔV); the slopes away from transformation (0.tr) can be expressed by the ratio of the coefficient of isobaric thermal expansion α to the isothermal compressibility χ :

$$\left(\frac{dP}{dT}\right)_{0.tr} = \frac{\alpha}{\chi} \quad (1)$$

At second-order transitions, only the thermodynamic coefficients α and χ undergo discontinuities without changes of molar volume or entropy. The transformation will be detected by a simple change of slope (25), the coordinates of which are the transition temperature and pressure. The set of these points, recorded on a P-T phase diagram, is used to plot the lines of phase equilibrium, the slopes of which are governed by Ehrenfest's relation.

In vitreous transitions, the transition from the low-temperature phase to the high-temperature phase occurs without discontinuity and gradually over a few degrees. The vitreous (glass) transition temperature (T_g) and pressure (P_g) are obtained at the point of intersection of the straight parts corresponding to the single-phase system.

Since the experiment is performed under well-defined thermodynamic conditions, the thermobarograms are independent of the rate of heating or cooling. Temperature cycles were used to test the suitability for densification of the samples (presence of hysteresis in the thermobarogram).

Principle of Thermodilatometric Analysis

Thermodilatometric analysis (26) is performed on the interference figure obtained at the surface of a sample when it is used as one of the mirrors of a Michelson interferometer. Concentric rings that represent the curves of equal thickness are observed. When the temperature of the sample is made to vary, the resulting variation of volume is reflected by a movement of the interference rings. The changes of intensity of the central fringe are recorded versus temperature to detect transitions by sudden or gradual variations of the speed of movement. It is then possible to determine the coefficient of thermal expansion (α) and the variation of the molar volume (ΔV).

The apparatus used for thermobarometry and thermodilatometric analysis has been described by Buisine et al. (26); the temperature domains accessible are, respectively, from -40° to $+270^\circ\text{C}$ and from $+20^\circ$ to $+90^\circ\text{C}$ (at atmospheric pressure); the heating and cooling rates used are $1^\circ\text{C}/\text{min}$ and $5^\circ\text{C}/\text{min}$, respectively. Both methods can be used to determine the thermodynamic quantities α and χ , the values of which are given for five bitumens in Table 4.

TABLE 4 Thermodynamic Data for the SHRP Bitumens

AAC1										
T °C	-17.5	-2.5	+8	+10		+30		+42		+54
α				←	4.0	→	←	5.9	→	←
χ_h								4.9		9.8
χ_c								5.9		9.0
AAD1										
T °C			+5		22		36		55	
α						←	9.4	→	←	10.3
χ_h							9.3		11.9	
χ_c							10.0		12.0	
AAG1										
T °C	-7	0				28		38		
α		←		3.6		→	←	4.1	→	←
χ_h								3.6		2.9
χ_c								3.6		2.9
AAK1										
T °C	+4	13	22		30		51		60	64
α			←	8.2	→	←	7.3	→	←	4.4
χ_h							5.3		5.57	
χ_c							5.4		5.25	
AAM1										
T °C	-7	6					44			
α		←			11.1	→	←	11.7	→	
χ_h							9.1		17.5	
χ_c							12.0		12.7	

Transition temperature T (°C), coefficient of isobaric thermal expansion α (10^{-4}C^{-1}), coefficients of isothermal compressibility during heating χ_h and cooling χ_c (10^{-10}Pa^{-1}).

It will be noted that for the five samples analyzed, the P-T phase diagrams consist of many domains where the coefficients of pressure α/χ are stable; their characteristic temperatures are given in Table 4. This means that changes in the properties of the material are detected (26) that can be ascribed to changes of phases that are beginning or ending.

Under the conditions of analysis, only bitumen AAC1 exhibits a vitreous transition at -17.5°C ; for the other bitumens the domain is not accessible. It will, however, be noted that

- AAG1 and AAM1 have few domains (two or three),
- AAK1 and AAC1 show the largest number of transformations, and

- AAK1 and AAD1 have several practically identical domains of stability of composition.

The temperature cycles applied reveal that the bitumens behave differently; thermal hysteresis may or may not be observed (Figure 5). For example,

- AAG1 has a very flat cycle, whereas AAM1 exhibits a very marked hysteresis;
- The thermal cycles of bitumens AAK1, AAD1, and AAM1 have two quite distinct parts; the pressure obtained during heating is always greater than that obtained during cooling, which means that there has been densification, since the sample occupies a smaller volume during cooling; and

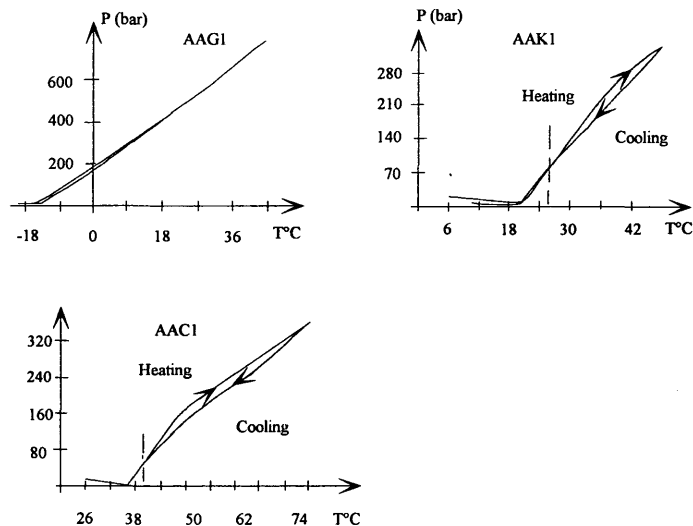


FIGURE 5 Thermobarograms of AAG1 (two consecutive thermal cycles), AAK1 (one thermal cycle), and AAC1 (two consecutive thermal cycles).

• Several consecutive cycles with no resting time were performed; they failed to detect any accumulation of densification.

The thermodilatamicroscopic measurements also showed that the coefficient of thermal expansion α in a domain of stability does not change during the heating and cooling cycles. Thus the existence of hysteresis results from the variation of the coefficient of compressibility χ in the course of the temperature cycle.

DIFFERENTIAL SCANNING CALORIMETRY AND THERMOMICROSCOPY

Differential calorimetric analysis is used at constant pressure to determine the behavior as a function of temperature. The detection of a thermal effect will be the sign of a change in the properties of the material studied. Previous studies had already shown the importance of thermal relaxation and of the type of gases adsorbed to the repeatability of endothermal effects (27), whereas other research has determined the origin of these effects by correlating them with the presence of the crystallized fraction (CF) of saturated derivatives and proposing a rapid assay method (28). "Crystallized fraction" refers to any constituent that precipitates or crystallizes by simple cooling of the sample. Paraffins are elements of this fraction, and it has been observed that bitumens derived from crudes that are paraffinic or are very sensitive to temperature have a high level of crystallized fractions. The study of SHRP bitumens was presented in Rome in 1991 (29).

Differential Scanning Calorimetry

Thermograms are obtained between -100°C and $+100^{\circ}\text{C}$ at a heating rate of $5^{\circ}\text{C}/\text{min}$. Whatever bitumen is studied (SHRP or others), the DSC profile shows the following features:

1. At low temperature an increase of the thermal capacity extending over approximately 30° , corresponding to the vitreous transition of the hydrocarbon matrix, and correlated with the Fraass brittleness point (29,30);
2. Two endothermal masses of more or less large amplitude at temperatures between -5° and $+90^{\circ}\text{C}$ caused by the dissolution of the fractions that have crystallized during cooling; the content of the crystallized fractions has been correlated with the difference in the linear variation of viscosity versus temperature shown in Heukelom's diagram (for a straight-run bitumen, not paraffinic and not blown) (30);
3. Beyond 90°C , no further significant evolution of the signal.

Table 5 gives the thermal parameters T_g and CF of the various SHRP bitumens.

The storage temperature of the samples (after 24 hr) affects both the CF content and the DSC profile of the bitumens (32). Although two effects can be observed after storage at 25°C , three masses appear after storage at -30°C . This applies to the eight SHRP bitumens generally, and the CF content passes through a maximum for a storage temperature of -15°C .

TABLE 5 Thermal Parameters T_g and CF of SHRP Bitumens

Name	T_g $^{\circ}\text{C}$	CF %	% Paraffins LCPC
AAA1	-24.8	0.5	
AAB1	-27.3	4.6	2.7
AAC1	-25.7	4.9	
AAD1	-28.8	1.6	
AAF1	-24.6	3.6	
AAG1	-5.2	0.2	
AAK1	-22.8	1.2	
AAM1	-24.8	5.2	3.2

Thermomicroscopy

Observation of bitumens in thermomicroscopy (30) is by phase contrast microscopy (Zernick's method) or in polarized light (the most widely used method). The two methods can be combined to characterize highly or slightly crystallized objects in an amorphous matrix and to distinguish the differences between nonmiscible liquid phases and precipitation-crystallizations in the solid phase.

The SHRP bitumens have a low CF content. As has already been shown (30), at CF levels below 6 percent, observation both by phase contrast and by polarization is delicate. On the other hand, the addition of *n*-alkanes, alone or in a mixture, or more generally of saturated fractions to bitumen AAG1 leads to the appearance of organized zones of small size (4 to $6\ \mu\text{m}$) similar to those that can be observed in a bitumen that has a high CF content or a distillation residue (31).

An interpretation of the endothermal masses has been proposed (29,30): the time and temperature dependence of the thermal effects can be ascribed not to the change of crystalline type but to the change of the type of liquid phase; there would therefore seem to be two coexisting liquid phases at ambient temperature. This result is important for the generation of a model of bitumen and may change the way results (rheological results, for example) are interpreted. It would therefore seem that bitumens at ambient temperature have at least two phases.

DISCUSSION OF RESULTS

The results presented here must be interpreted in two respects: composition and physicochemical structure, and mechanical behavior.

Volatility is a criterion that merits special attention because the method proposed can also be used to solve practical problems such as identifying the origin of pollution, a problem difficult to handle by conventional methods.

The comparison of the analysis by generic group and by GPC shows that the index of colloidal instability (CI) governs the agglomeration of asphaltenes, and thus GPC classifies bitumens into three types. In addition, CI, being correlated with the width of the relaxation spectrum, has a direct influence on rheological behavior. Furthermore, the presence of entities likely to evolve with the temperature (clusters and CF, molten or in nonmiscible fluid equilibrium) can entail a difference in the laws of time-temperature transposition (non-unicity of Black's curve). The correlation is well satisfied by bitumens AAM1 and AAB1 and less well by bitumens AAC1 and AAF1; bitumen AAG1, practically perfect in unicity, has no CF; for bitumens AAA1, AAD1, and AAK1, with a low

level of CF, nonunicity is observed at high temperatures. These results mean that the rheological behavior is governed in a complex way by the chemical composition and phase equilibria. This complexity of the thermomechanical behavior is confirmed by the thermal analysis.

Artificial aging by the RTFOT implies chemical changes that can be tracked by SEE fluorescence. It causes, in addition to the changes that are systematically observed (penetrability, softening temperature, GPC, complex modulus), a greater evolution of the most condensed aromatic rings (five rings). However, bitumen AAM1 here again exhibits a behavior of its own (large evolution and practically unique species of aromatic rings). Bitumens AAF1, AAG1, AAK1, and AAM1 belong to classes that in France would be used in hot mixes. Although they meet the French specifications, their kinetic and thermal sensitivities are high and might therefore lead, without special formulation precautions, to nonnegligible permanent strains.

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