

STRUCTURAL UNITS OF MALTENES AND ASPHALTENES FROM HYDROGENATION OF COAL

IVO LANG

*Institute of Geology and Geotechnology,
Czechoslovak Academy of Sciences, 182 09 Prague 8*

Received March 18th, 1981

The calculation of the unit structure weight (USW) from NMR data is discussed. A comparison with the average molecular weight (\bar{M}_r) values from vapour phase osmometry and mass spectrometry measurements showed that for the coal maltenes investigated (the fraction from the coal hydrogenation product soluble in pentane), USW can be looked upon as a rapid approximation of \bar{M}_r . For asphaltenes, the calculation of USW is to a high extent dependent upon the assumed arrangement of the aromatic system. For an approximation of \bar{M}_r of the asphaltenes studied, the most satisfactory was the calculation of USW from the parameters of the Williams method assuming the occurrence of a *peri-cata*-condensed system. The USW of coal hydrogenation products calculated from NMR (^1H and ^{13}C) spectra should not be attributed the physical meaning of their smallest building units.

Coal liquefaction products separate by solvent fractionation into maltenes (low-molecular oils and resins, fraction soluble in pentane) and asphaltenes (fraction soluble in benzene and insoluble in pentane). Low-molecular oils are the desired products from the coal liquefaction, while asphaltenes, occurring as intermediates, cause troubles in the industrial process. There are also troubles in choosing the appropriate methods for the technological process control, involving, *e.g.*, determination of the relative molecular weight of the products and intermediates. The coal extracts and asphaltic bitumens are of polydisperse nature, as proved by a number of techniques^{1,2}, recently particularly by gel chromatography. Different methods of determination of the mean molecular weight (\bar{M}_r) of bitumens afford very different values; for petroleum asphaltenes, for instance, values have been published covering a span of three orders of magnitude²⁻⁴.

The differences are in part accounted for by the definition of the mean value². The numerical average, $\bar{M}_n = \sum M_i N_i / \sum N_i$ (M_i is the relative molecular weight and N_i is the number of particles of the i -th component), is invariably lower than the weight average, $\bar{M}_w = \sum M_i^2 N_i / \sum M_i N_i$, and the difference is the higher the wider is the span of molecular weights covered by the bitumenic system.

To the most part, however, the differences arise from the association of the bitumenic particles in the conditions of the experiment^{5,6}; in fact, the aggregation state may be different in different solvents and dependent on the concentration and other circumstances. As pointed out by Winni-

ford⁵, methods in which the aggregates are not broken down by high pressure stress, temperature, or shaking afford noticeably high \bar{M}_r values for bitumens.

Particle association is the basis of Yen's concept of macrostructure of asphaltic substances^{5,7}, according to which various numbers of basic planar units (sheets) combine into spatial particles (cells), which in turn join into big associates — micelles. The conception of colloidal nature of asphaltenic bitumens is not new, of course, it dates back as far as the twenties and thirties of this century (e.g., ref.¹). In the model³, however, the various methods of determination of \bar{M}_r assume their specific positions: X-ray diffraction analysis and mass spectrometry serve for the determination of the unit structure weight, vapour phase osmometry is used for establishing the particle weight, while electron microscopy and ultracentrifugation are employed for studying the particle association into micelles.

Thus, Dickie and Yen³ used high-angle and low-angle X-ray diffraction for determination of the unit structure weight of petroleum asphaltenes and maltenes: from the number of the aromatic carbon atoms in the *peri*-condensed and *cata*-condensed aromatic systems, they calculated the weight of the aromatic lamellae (disk), and knowing the aromaticity value f_a they expressed the unit structure weight value as

$$\text{USW} = \text{aromatic lamellae weight}/f_a \quad (1)$$

The spectra of our coal asphaltenes did not allow us to apply this method⁸. This is a situation similar to that of Kim and Long⁹, who also failed in this respect, probably because the colloidal size of the coal asphaltenes was below the resolution of the unit used for the small-angle X-ray diffraction.

According to Dickie and Yen³, the fragments in the mass spectrum (70 eV) of asphaltene bitumens represent aromatic lamellae formed on the β -cleavage of the aliphatic and cyclanic bridges in the molecules, so that it is possible to calculate the average weight values of the lamellae. The authors³ verified the correctness of the method with a good result on a model mixture of polynuclear aromatic substances; the average values from the X-ray diffraction and mass spectrometry measurements were in a good mutual agreement.

An alternative way of determining the unit structure weight has been suggested by Haley¹⁰, who calculated the USW values of petroleum fractions from ¹H NMR data. Knowing the hydrogen-to-carbon atomic ratio for the hypothetical unsubstituted aromatic system, the Brown-Ladner $H_{\text{aru}}/C_{\text{ar}}$ parameter¹¹, Haley interpolated the number of the aromatic carbon atoms per structural unit, C_{AS} , from the table of the theoretical aromatic hydrogen-to-carbon ratios for the assumed *peri*-condensed systems¹⁰. If the aromaticity f_a is known, the average USW value can then be calculated as

$$\text{USW} = 1200C_{\text{AS}}/C_{\text{c1}}f_a \quad (2)$$

where C_{c1} is the carbon content (% wt.) obtained from elemental analysis.

For a general application of this method, however, the assumption of the *peri*-condensed system is questionable. Williams¹² has suggested a relation for the calculation of C_{AS} , in which the assumption of the *peri*-condensed system is slightly corrected for the possible occurrence of *cata*-condensed structures:

$$C_{\text{AS}} = 7(C_{\text{A}}/C_1)^2 - 1 \quad (3)$$

where C_1 is the number of non-bridge carbon atoms of the aromatic rings and C_{A} is the total number of aromatic carbon atoms. As follows from the definition of the parameters, the Brown-Ladner $H_{\text{aru}}/C_{\text{ar}}$ parameter and the Williams C_1/C_{A} parameter are equivalent. The relation (3)

has been used, for instance, by Dereppe and coworkers¹³. The correction for the *cata*-condensed lamellas is, however, the smaller, the less than 0.8 is C_1/C_A , and does not apply at all for $C_1/C_A > 0.8$; so the relation (3) suits mainly for a rapid and approximate orientation.

A mean *peri-cata*-condensed model has been proposed by Ali¹⁴, while the assumption of exclusively *cata*-condensed aromatic lamellas in the structure of coal asphaltenes has been used in the work of Kanda and coworkers¹⁵.

We applied the above methods of determination of the unit structure weight to a study of maltenes and asphaltenes isolated from autoclave hydrogenation products of some Czechoslovak coals. Having failed in the use of X-ray diffraction, we compared the USW values obtained from ¹H and ¹³C NMR data under various assumptions of the aromatic system structures with the values from mass spectrometry and vapour phase osmometry measurements.

EXPERIMENTAL

The coal maltenes (M) and asphaltenes (A) were isolated from hydrogenation products of Czechoslovak brown coal 1) North-Bohemian region, Koh-i-noor mine; 2) Northwest Bohemian region, Silvestr mine) and bituminous coal (Ostrava-Karviná Mining Area: 3) Paskov mine, 4) Hlubina mine, 5) ČSA mine). The dried coal was hydrogenated with hydrogen for 3 h in a rotary autoclave at 400°C and 20 MPa in the presence of 1% wt. (NH₄)₂MoO₄ catalyst. The product was extracted with benzene in a Soxhlet apparatus, benzene was evaporated, and maltenes were extracted from the evaporation residue by pentane¹⁶.

The ¹H NMR spectra were scanned on a Varian XL-100 instrument at 37°C; 10% solutions in CDCl₃ (Merck) were measured, and tetramethylsilane (TMS) was used as the internal standard.

The ¹³C NMR spectra were measured on a Bruker WP-80 FT NMR spectrometer working with a deuterium internal stabilization system and a broadband proton decoupler. The samples were prepared as 2.5% wt. (A) or 10% wt. (M) solutions in CDCl₃ and measured in 10 mm cells at 37°C. Internal standard TMS, conditions: number of points 8 k, pulse width 3 μs (35°), measurement offset 200 ppm, decouple offset 5 ppm, AQT 0.546 s, spectrum width 7 500 Hz, number of scans 3 000. The spectra were quantitatively evaluated by using the broadband proton decoupling, by addition of a relaxation reagent (ferric acetylacetonate (supplied by K & K)), and by combination of both techniques^{16,17}.

The elemental composition of the coal maltenes and asphaltenes is given in Tables I and II, respectively, the proton and carbon type distribution in the ¹H and ¹³C NMR spectra for the maltenes and asphaltenes are given in Tables III and IV, respectively.

Vapour phase osmometry (VPO) was employed for the determination of the relative molecular weight in tetrachloromethane, benzene, chloroform, tetrahydrofuran, pyridine, and nitrobenzene, respectively. The measurements were carried out at least at two temperatures on a Knauer instrument calibrated with squalane. The samples were measured at three or four concentrations in each solvent, and evaluated by extrapolation to infinite dilution¹⁸.

The mass spectra were measured using the ionizing electron energy 10 eV. Maltenes were injected into the heated reservoir (200°C) of an LKB 9000 instrument; asphaltenes were sublimed directly into the ion source of an AEI MS 902 spectrometer, the spectra were scanned with gradual heating of the sample from 20°C to 400°C.

RESULTS AND DISCUSSION

As mentioned above, Haley's method¹⁰ of calculation of USW requires the knowledge of the f_a and C_1/C_A structure parameters, which can be calculated from the ¹H NMR data by the today classic methods of Brown and Ladner¹¹ or of Williams¹². If the elemental composition is known and some assumptions hold true, these methods allow the quantitative record of the proton NMR spectrum to be interpreted in terms of several structural parameters of the bitumenic sample.

The Brown-Ladner method¹¹ has been employed most frequently in studies of coal hydrogenation products. In some cases it turned out^{19,20,16} that the principal aliphatic component was not methylene groups, as is assumed in the method ($x = y =$

TABLE I
Elemental composition of the coal maltene samples

Element	Content, % wt.				
	M1	M2	M3	M4	M5
C	87.44	88.72	88.98	88.92	88.51
H	9.14	9.68	8.55	8.14	8.55
N	0.58	0.26	0.87	0.57	0.58
S	0.30	0.78	0.40	0.70	0.28
O ^a	2.54	0.56	1.20	1.67	2.08

^a Calculated as the difference.

TABLE II
Elemental composition of the coal asphaltene samples

Element	Content, % wt.				
	A1	A2	A3	A4	A5
C	89.85	89.98	90.14	90.81	89.89
H	5.86	6.30	5.85	1.18	1.29
N	1.33	0.63	1.18	1.29	0.75
S	0.31	0.69	0.47	0.55	0.32
O ^a	2.65	2.40	2.36	1.32	2.53

^a Calculated as the difference.

= 2, Table V), and consequently the results contain a systematic error. ^{13}C NMR spectroscopy permits the aromaticity f_a to be determined directly from the spectrum, whereupon the x , y , and C_1/C_A (or $H_{\text{aru}}/C_{\text{ar}}$) parameters from the original Brown-Ladner method can be refined. This is the basis of the combined ^{13}C - ^1H method. The equations relevant for the calculation of the f_a and C_1/C_A parameters by the Brown-Ladner¹¹ and Williams¹² methods are listed in Table V.

Table VI gives the average vapour phase osmometry \bar{M}_r values in benzene (37, 45, and 60°C), the mass spectrometry data, and the USW values calculated by the above

TABLE III

Distribution of the proton and carbon types in the ^1H and ^{13}C NMR spectra of the coal maltene samples

Atoms	Sample				
	M1	M2	M3	M4	M5
H_{ar}^*	0.2545	0.1971	0.3410	0.3462	0.3312
H_{α}^*	0.2680	0.2601	0.3151	0.3228	0.2867
H_{β}^*	0.3410	0.3888	0.2474	0.2331	0.2766
H_{γ}^*	0.1367	0.1526	0.0966	0.0967	0.1057
C_{ar}^*	0.510	0.463	0.617	0.636	0.575
C_{al}^*	0.490	0.537	0.383	0.364	0.425

TABLE IV

Distribution of the proton and carbon types in the ^1H and ^{13}C NMR spectra of the coal asphaltene samples

Atoms	Sample				
	A1	A2	A3	A4	A5
H_{ar}^*	0.4412	0.4045	0.4612	0.4741	0.5030
H_{α}^*	0.3003	0.3207	0.3256	0.3192	0.2894
H_{β}^*	0.1886	0.2081	0.1600	0.1474	0.1566
H_{γ}^*	0.0698	0.0667	0.0533	0.0593	0.0510
C_{ar}^*	0.745	0.719	0.759	0.760	0.758
C_{al}^*	0.255	0.281	0.241	0.240	0.242

three NMR methods. The data are in a satisfactory agreement. A maltene structural unit corresponds to the average molecule. In addition to other structural parameters, it is possible to determine directly the molecular weight of an average molecule from the NMR spectrum. This is of a particular value if the quantity of the sample is not sufficient to enable vapour phase osmometry measurements at several concentrations; the VPO technique is not a straightforward one, and an entirely incorrect \bar{M}_r value may result from measurement at a single concentration.

The calculation of \bar{M}_r of maltenes from the Brown-Ladner ^1H and ^{13}C - ^1H parameters affords practically identical values, so that after verification, the ^{13}C NMR

TABLE V
Calculation of the f_a and C_1/C_A parameters from the ^1H NMR data_a

Brown-Ladner method ¹¹	Williams method ¹²
$f_a = \frac{C/H - H_\alpha^*/x - (H_\beta^* + H_\gamma^*)/y}{C/H}$	$n = (H_\alpha^* + H_\beta^* + H_\gamma^*)/H_\alpha^*$
	$f = 12n/(2n + 1 - 2r)$
	$C_S = f(H_\alpha^* + H_\beta^* + H_\gamma^*) H_{e1}$
$H_{aru}/C_{ar} = \frac{H_\alpha^*/x + H_{ar}^* + (O + N + S)/H}{C/H - H_\alpha^*/x - (H_\beta^* + H_\gamma^*)/y}$	$C_1 = (12H_{ar}^* + fH_\alpha^*) H_{e1}$
	$C_A = C_{e1} - C_S$
	$f_a = C_A/C_{e1}$
$[H_{aru}/C_{ar} = C_1/C_A]$	

TABLE VI
The \bar{M}_r and USW values of the maltene samples

Maltenes	\bar{M}_r		USW		
	VPO benzene	MS	Brown-Ladner ¹¹	Williams ¹²	^{13}C - ^1H NMR (ref. ¹⁹)
M1	210	160	200	240	180
M2	220	190	230	280	220
M3	190	160	160	200	160
M4	180	210	180	210	180
M5	200	170	180	210	150

spectra need not be measured any more. The data from the Williams method parameters are somewhat higher, because the method gives lower C_1/C_A ratios.

For asphaltenes, the average vapour phase osmometry \bar{M}_r values in several solvents and in benzene, \bar{M}_r values obtained from mass spectra measurements, and the USW data derived from the NMR spectra are given in Table VII. The USW values calculated by the ^{13}C — ^1H method are invariably slightly lower than those obtained by the classical Brown-Ladner method.

The USW data in Table VII document how the values are dependent on the assumed arrangement of the aromatic rings in the substance. Difficulties start to arise with anthracene ($M_r = 178$) and become more pronounced as the number of rings increases. As long as the occurrence of phenyl bonds can be considered likely (and the mass spectra of our sample confirm it), it is, in fact, impossible to set up a universal dependence of the C_1/C_A parameter and the number of aromatic carbon atoms C_{AS} , as depicted in Fig. 1.

In order for us to be able to calculate correctly the basic structural unit of complex substances, we must know in advance the number of rings and the way of their joining. Similar problems are inherent also in other methods of determination of the average bitumenic structure size. In osmometry, similarity between the standard and the sample under study with respect to the size, structure, and properties of the molecules is not a negligible factor. This, however, means that "in order to learn we have to know". Mass spectrometry affords correct \bar{M}_r values of bitumens provided that the sample is evaporated in the source completely. In the case of the A1—A4 asphaltenes, 10–20% wt. remained unevaporated, the residue possessing the highest

TABLE VII
The \bar{M}_r and USW values of the asphaltene samples

Asphaltenes	\bar{M}_r			USW				
	VPO ^a	VPO benzene	MS	Brown-Ladner ¹¹			Williams ¹²	
				<i>peri</i>	<i>peri-cata</i>	<i>cata</i>	<i>peri</i>	<i>peri-cata</i>
A1	550	570	370	320	400	580	380	490
A2	510	500	470	280	340	430	360	450
A3	550	570	380	290	340	440	370	470
A4	540	560	420	260	300	370	320	400
A5	310	320	390	210	220	230	230	270

^a Average value from determinations in CCl_4 , C_6H_6 , CHCl_3 , THF, and pyridine.




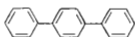
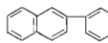
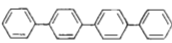
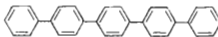

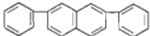
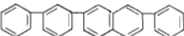
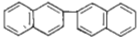

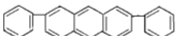

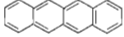
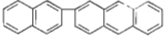

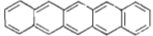

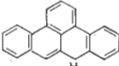

C_1/C_A		C_{AS}
1.0		6
0.83		12
0.80		10
0.78		18
0.75	 	16, 24
0.73		 30
0.71	  	14, 22, 28
0.70		 20
0.69		 13, 26
0.67	  	12, 18, 24
0.64		 24
0.64		 22
0.63		 16
0.62		 21
0.60		 20

FIG. 1

Non-bridge-to-total carbon ratio C_1/C_A and the number of carbon atoms C_{AS} of the basic aromatics with one through five aromatic rings

(and unknown) \bar{M}_r . The true \bar{M}_r values can be thus expected to be accordingly higher than the MS data given in Table VII. The calculation of USW data from the fragments in the 70 eV spectrum will be affected likewise. The structural unit was determined³ assuming that the phenyl bonds and other bridges were cleaved, which is questionable; and certainly this assumption is not satisfied in the conditions of the NMR measurements. Obviously, the USW calculation and the conventional considerations concerning the number of repeating units in an average bitumen molecule are of speculative nature. We suppose that the USW values derived from NMR data can only serve as an approximation of the molecular weight of an average molecule. For verified sample series this approximation is rapid and not too demanding as far as the sample quantity is concerned, as discussed above. For the studied samples of coal asphaltenes, the best results were obtained by using parameters derived from the proton NMR spectrum by the Williams method¹² under the assumption of a *peri-cata*-condensed model for the samples. The *cata*-condensed model in conjunction with the Williams parameters led to high USW values. USW calculated from the NMR spectra of coal liquefaction products should not be associated with the physical concept of their smallest building units.

Thanks are due to Dr J. Mitera, Prague Institute of Chemical Technology, for the mass spectra measurements and discussion of the results.

LIST OF SYMBOLS

C_A	total number of aromatic carbon atoms
C_{AS}	number of aromatic carbon atoms per structural unit
C_S	carbon fraction in the saturated substituents
C_{al}^*	relative abundance of aliphatic carbon atoms in the ^{13}C NMR spectrum
C_{ar}^*	relative abundance of the aromatic carbon atoms in the ^{13}C NMR spectrum
C_{e1}, H_{e1}	content of the elements (% wt.)
C_1	number of the non-bridge aromatic carbon atoms
f	average C/H weight ratio in the alkyl groups
f_a	aromaticity, ratio of the number of aromatic carbon atoms to the total number of carbon atoms
$f_a(^{13}\text{C}) = C_{ar}^*$	
H_{aru}/C_{ar}	ratio of the number of aromatic hydrogen atoms to the number of aromatic carbon atoms for a hypothetical unsubstituted aromatic system
H_i^*	$= H_i / \sum_i H_i$, relative abundance of the proton type; $i = ar$ (9–6 ppm), α (4–2 ppm), β (2–1 ppm), γ (1–0.5 ppm)
\bar{M}_r	relative molecular weight of an average molecule
n	average number of carbon atoms per alkyl substituent
r	number of cyclanic rings per alkyl substituent
USW	unit structure weight
x	$= H_\alpha / C_\alpha$, average number of protons per a carbon atom in the α position with respect to the aromatic rings
y	$= (H_\beta + H_\gamma) / (C_\beta + C_\gamma)$, average number of protons per a carbon atom in the β and γ positions with respect to the aromatic rings

REFERENCES

1. van Krevelen D. W.: *Coal*, Chapter X. Elsevier, Amsterdam 1961.
2. Witherspoon P. A., Winniford R. S. in the book: *Fundamental Aspects of Petroleum Geochemistry* (B. Nagy, U. Colombo, Eds). Elsevier, Amsterdam 1969.
3. Dickie J. P., Yen T. F.: *Anal. Chem.* **39**, 1847 (1967).
4. Moschopedis S. E., Fryer J. F., Speight J. G.: *Fuel* **55**, 227 (1976).
5. Winniford R. S.: *J. Inst. Petrol.* **49**, 215 (1963).
6. Wales M., Van der Waarden M.: *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.* **9**, B21 (1964).
7. Yen T. F.: *Chemistry of Asphaltene in Coal Liquids*. Preprint of Univ. of Southern California 1977.
8. Hrnčíř J., Spitzer Z.: Private communication.
9. Kim H., Long R. B.: *Ind. Eng. Chem. Fundam.* **18**, 60 (1979).
10. Haley G. A.: *Anal. Chem.* **43**, 371 (1971).
11. Brown J. K., Ladner W. R.: *Fuel* **39**, 87 (1960).
12. Williams R. B.: *ASTM Spec. Tech. Publ. No 224* (1958); *Spectrochim. Acta* **14**, 24 (1959).
13. Dereppe J. M., Moreaux C., Castex H.: *Fuel* **57**, 435 (1978).
14. Ali L. H.: *Fuel* **50**, 298 (1971).
15. Kanda N., Itoh H., Yokoyama S., Ouchi K.: *Fuel* **57**, 676 (1978).
16. Lang I., Hájek M., Sklenář V., Vavrečka P., Němec J.: *Chem. Prům.* **29**, 634 (1979).
17. Sklenář V., Hájek M., Šebor G., Lang I., Suchánek M., Starčuk Z.: *Anal. Chem.* **52**, 1794 (1980).
18. Lang I., Vavrečka P., Weishauptová Z., Šebor G., Hájek M.: *Chem. Prům.* **30**, 639 (1980).
19. Retcofsky H. L., Schweighardt F. K., Hough M.: *Anal. Chem.* **49**, 585 (1977).
20. Retcofsky H. L.: *Appl. Spectrosc.* **31**, 116 (1977).

Translated by P. Adámek.