A RE-INVESTIGATION OF DENSIMETRIC METHODS OF RING ANALYSIS

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For many years the chemist has sought a method whereby the average structural character of the molecules in a complex mixture might be determined. In general, two types of mixtures have received most attention. One has consisted of mixtures of compounds comprising a relatively narrow molecular weight range and where the average molecular weight could be obtained; examples are narrow boiling cuts from petroleum. The second has consisted of very complex systems, such as coals, where molecular weight could not be determined, and, indeed, where the concept of molecular weight might not be applicable.

Present studies in this laboratory have as their objective clarification of the structure of the asphaltic, non-hydrocarbon constituents of crude oil and of the presumably similar, but higher molecular weight, black, insoluble organic fraction of ancient sedimentary rocks. From the point of view of structural type analysis, these substances represent a situation somewhere between that of a low molecular weight hydrocarbon mixture and the macromolecular structure of coals.

The development of procedures applicable to mixtures of known low molecular weight and to coals has taken place concurrently, many investigators contributing. Vlugter, Waterman, and van Westen[1] were among the first to apply a system of ring analysis to complex hydrocarbon mixtures. van Nes and van Westen[2] continued the study, developing the n-d-M method primarily for petroleum oils. Using refractive index, density, and elementary analysis, van Krevelen[3], van Krevelen and Chermin [4], and van Krevelen and Schuyer[5] developed a somewhat similar method of statistical analysis, applicable to coals and other substances where molecular weight could not be obtained. Smith[6] and Montgomery and Boyd[7] elaborated on both methods to obtain further structural parameters, testing the methods using data for a variety of pure hydrocarbon compounds as recorded by the American Petroleum Institute Research Project 42. Good agreement was obtained with respect to paraffins and naphthenes, but discrepancies were observed for the aromatics, particularly those consisting of fused rings. Dryden[8], working with coals, compared structural information derived from x-ray, nuclear magnetic resonance, and infrared data with comparable information calculated from the densimetric method of van Krevelen and found that agreement usually was poor.

Since the non-hydrocarbon constituents of the asphaltic fraction of crude oils and the insoluble organic residues obtained from ancient sediments, as well as of refinery asphalts, are believed to contain both aliphatic and aromatic fused ring groups, a re-investigation of the densimetric methods of ring analysis was considered justified.

(1) J. Inst. Petrol. Tech., 18, 735 (1932); Ibid., 21, 661 (1935).
(2) "Aspect of the Constitution of Mineral Oils," Elsevier, New York, 1951.
(3) Brenn. Chem., 34, 167 (1953).
(4) Fuel, 33, 79 (1954).
(5) "Coal Science," Elsevier, New York, 1957.
(6) Ohio State Univ. Bull., 152, 1 (1953).
(7) Anal. Chem., 31, 1290 (1959).
(8) Fuel, 37, 444 (1958).

For mixed aliphatic-aromatic compounds or mixtures thereof where the molecular weight could be determined, the following equations have been proposed by van Krevelen:

$$(1) \qquad \frac{M}{\rho} = \sum_i n_i V_i - K_M$$

where:

$$(2) \qquad K_M = V_R R$$

M = molecular weight of the compound or mixture,
ρ = the density,
n_i = the number of the i th atomic species,
V_i = Traube's atomic volumes,
K_M = molar volume contraction,
V_R = molar volume contraction per ring,
R = number of rings.

For aliphatic compounds or mixtures, K_M is approximately zero.

To cope with substances such as coal where molecular weight is very high or cannot be determined, the equation was converted to the form:

$$(3) \qquad \frac{1200}{\%C \cdot \rho} = \sum_i n_i V_i / C - V_R \cdot \frac{R}{C}$$

where %C is the per cent carbon obtained by elementary analysis and C is the number of carbon atoms in the structural unit.

To calculate the average number of rings per molecule, R, from equations (1) and (2) or the number of carbons per ring, C/R, from equation (3), it is necessary to evaluate V_R. Using three reference substances, namely, cellulose where R = 0, polystyrene where R = 1, and graphite where R = ∞ van Krevelen and Chermin derived the empirical relation:

$$(4) \qquad V_R = 9.1 - 3.6 \frac{H}{C}$$

where H is the number of hydrogen atoms.

Relations (1) and (3) thus become:

$$(5) \qquad R = \frac{9.9C + 3.1\,H + \ldots - \frac{M}{\rho}}{9.1 - 3.6 \frac{H}{C}}$$

and

$$(6) \qquad \frac{C}{R} = \frac{9.1 - 3.6 \frac{H}{C}}{9.9 + 3.1 \frac{H}{C} + \ldots - \frac{1200}{\%C \cdot \rho}}$$

Equation (6) was used to calculate the number of carbons per ring for a native asphaltene prepared in this laboratory from a Lagunillas crude oil and for two carbon blacks studied by Kuroda[9]. In Table I, Part A, the values obtained (underlined) are compared with values derived from infrared, nuclear magnetic resonance, and x-ray data. The numerical results indicate that the values of C/R calculated by means of equation (6) are too low.

(9) J. Colloid Sci., 12, 496 (1957).

Testing of equation (5) with compounds of known structure indicated that the expression for V_R, equation (4), probably was in error. That this relationship was empirical and disputable was recognized, of course, by van Krevelen. Rather than being a function of H/C, V_R appeared to be a constant for systems comprising three or more fused rings. To test the theoretical implications of this conclusion, an attempt has been made to derive from basic assumptions an expression for V_R.

In order to treat the problem of a condensed ring aromatic system, i.e., of a hexagonal network in two dimensions, it is necessary to assume some sort of model. A number of models are possible, e.g., a circle, exemplified by coronene; a square, by anthrodianthrene; a triangle, by perinaphthindene; and a rectangle, by perylene. For all these models, however, the number of rings can be expressed as a function of the number of aromatic carbon atoms and the number of aromatic hydrogen atoms by the equation:

$$R = 1 + \frac{C_A - H_A}{2} \tag{7}$$

where:

$$H_A = p\, C_A^{1/2} - q \tag{8}$$

In the latter equation the values of p and q vary with the model. Of the various possible models, the rectangular was selected for development of an expression for V_R.

If an aromatic cluster is designated as [m,n] according to the method of Coulson[10] where m denotes the number of biphenyl type rings, i.e., along the x axis, and n the number of naphthalene type rings, i.e., along the y axis, then:

$$H_A = 2(2m + n) \tag{9}$$

$$C_A = 2m(2n + 1) \tag{10}$$

and the number or rings as:

$$R = 2mn - m - n + 1 \tag{11}$$

Now, solving equation (11) in terms of H_A and C_A, equation (7) is obtained. Since long chains of condensed aromatic rings are seldom encountered in stable molecules, the simplified approximation is made that:

$$m \leq n \tag{12}$$

Now, H_A can be expressed in terms of C_A and after simplifying,

$$H_A = 3C_A^{1/2} - 3/2 \tag{13}$$

or

$$R = 0.5\, C_A - 1.5\, C_A^{1/2} + 1.75 \tag{14}$$

If the general equation (1) is applied to an aromatic cluster and the terms transposed,

$$K_M = \sum_i n_i V_i - M/\rho_A \tag{1a}$$

Substituting Traube's values for $\sum_i n_i V_i$ and the value of M:

$$K_M = 9.9C_A + 3.1H_A - (12C_A + H_A)\rho_A^{-1} \tag{15}$$

(10) "Proceedings of the Conference on Carbon," held at the University of Buffalo, Symposium Publication Division, Pergamon Press, New York, 1958.

To proceed further, it is necessary to evaluate ρ_A in terms of C_A. This step has been achieved through the following derivation -

In the case of a two-dimensional hexagonal net the area of the equilateral triangle formed by joining the centers of three adjacent rings can be expressed as:

$$(16) \qquad \Delta = 3\sqrt{3} \cdot a^2/4$$

If the net is comprised of aromatic carbon atoms, a is the bond distance and Δ the area occupied by one carbon atom. For a system consisting of uniformly stacked sheets, the minimum interlayer distance is 3.34 Å and hence the maximum density, 2.28 g./cm.^{3}.

Now it can be seen from Figure 1 that for aromatic hydrocarbons the density can be related to the number of carbon atoms by means of the equation:

$$(17) \qquad \frac{2.28}{\rho} - 1 = a\, C_A^{\,b} .$$

Although this equation is considered empirical at present, there appears to be theoretical evidence to support it. The plotted points in the figure represent nine aromatic hydrocarbons of known structure and the two carbon blacks cited in Table I, Part A. From the resulting straight line, the intercept, a, and the slope, b, can be evaluated as follows:

$$a = 3.15$$
$$b = -0.5$$

and equation (17) becomes:

$$(18) \qquad \rho_A^{-1} = 0.44 + 1.38\, C_A^{-1/2}$$

With an expression for ρ_A in terms of C_A, it is possible to continue development of the relationship expressed by equation (15). Substituting the values of H_A for equation (13) and ρ_A from equation (18), and dropping the small $C_A^{-1/2}$ term, equation (15) becomes:

$$(19) \qquad K_M = 4.6 \quad -8.6\, C_A^{1/2} \quad -8.1$$

The final objective is to eliminate C_A by combining equation (19) with equation (14) and to substitute the resulting value of K_M in the general equation (1). Owing to the form of equations (19) and (14), a general solution for K_M in terms of R is difficult. Accordingly, the operation was accomplished graphically in Figure 2 by substituting arbitrary values of C_A into the equations and solving for R and K_M. The plotted points represent actual values for ten polynuclear aromatic hydrocarbons. The curve will be seen to be a straight line at large values of R but to become slightly concave upward at low R and does not quite pass through the origin. The slight curvature and failure to pass through the origin, of course, are not consistent with condition that K_M must be zero at R equal to zero. This is merely the result of the simplifying approximations that have been made.

The foregoing derivation shows that the assumption of V_R equal to a constant is entirely reasonable. To obtain the value of the constant, it is necessary only to replace the derived curve by its limiting slope.

Hence:

$$(20) \qquad V_R = \frac{K_M}{R} = 9.2$$

Similar derivations based on the circular, square, and triangular models lead to equations for H_A differing only slightly from that for the rectangular model, equation (13), as follows:

$$(21) \qquad \text{round} \qquad H_A = 2.46\ C_A^{1/2}$$

$$(22) \qquad \text{square} \qquad H_A = 2.82\ C_A^{1/2} - 2$$

$$(23) \qquad \text{triangular} \qquad H_A = 3\ C_A^{1/2} - 1$$

As can be seen, all these equations yield curves closely approximating that shown in Figure 2 for the rectangular model, thus confirming the generality of the conclusion that V_R should be a constant. Whatever the model chosen, the numerical value of the constant is the same.

On the basis of the above results, it is proposed that the following equations be used for substances containing condensed ring systems:

$$(24) \qquad R = 0.11\ (9.9\ C + 3.1\ H + \ldots\ldots - \frac{M}{\rho})$$

where molecular weight can be determined and by:

$$(25) \qquad \frac{C}{R} = \frac{9.2}{9.9 + 3.1\ H/C + \ldots - \frac{1200}{\%C \cdot \rho}}$$

for substances where molecular weight cannot be determined.

In Table I, Part B, are presented new values of C/R for the petroleum asphaltene and carbon blacks, cited in Table I, Part A, this time calculated by means of equation (25). Referring to Part A, it will be seen that the values are in better agreement with the values derived from infrared, nuclear magnetic resonance, and x-ray than the values calculated by means of van Krevelen's equation (6).

In Table I, Part C, the values of C/R calculated by the two alternate methods are listed for the above asphaltene and for two others prepared from crude oils of widely different geographic origin. Values of density and elementary analysis are provided for comparison. It will be seen that the values of C/R computed by the method of van Krevelen and Chermin and by the modified method derived in this paper deviate not only in absolute value but also in trend. Further, it is interesting to note that the values of C/R calculated by the modified method do not vary as much with density and elementary analysis as do the values obtained by means of the van Krevelen equation, nor is there a direct correlation with density or the percentage of any single element.

In Tables II and III, equation (24) has been used to calculate values of R for a variety of compounds of known structure, using density values from the literature and values of C, H, etc., from the formulas. The compounds in Table II are unsubstituted aromatic hydrocarbons containing condensed ring systems. The compounds in Table III in many instances contain hetero elements and range from

aliphatic to cyclic systems containing substituted saturated and aromatic ring systems. The good agreement between the calculated R values and those indicated by the formulas is evident. It is concluded, therefore, that equation (25) will be dependable when applied to complex substances such as asphaltic fractions of crude oils and the black insoluble organic fraction of ancient sedimentary rocks.

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Table I

Values of C/R for A Native Petroleum Asphaltene and Two Commercial Carbon Blacks

Part A

Comparison of the Values Calculated by Means of the van Krevelen and Chermin Equation (6) with Values Obtained from Other Physical Measurements

Substance	Data From	Method	C/R Calculated
Asphaltene (Lagunillas)	infrared spectroscopy[1]	absorbance of the C-H stretching	5.7
	nuclear magnetic resonance[1]	proton type area	5.5
	x-ray[1]	(γ) and (002) bands	5.9
	x-ray[1]	(10) and (11) bands	4.2
	density-elementary analysis[1]	densimetric (van Krevelen and Chermin) Equation (6)	3.5
Royal Spectra	x-ray[2]	(10) band	2.9[3]
	density - H/C approximated from X-ray L_a values[2]	densimetric Equation (6)	2.1
Statex B	x-ray[2]	(10) band	2.6[3]
	density - H/C approximated from x-ray L_a values[2]	densimetric Equation (6)	2.1

Part B

Values Calculated by Means of Equation (25) Derived by the Authors

Substance	Data From	C/R Calculated
Asphaltene (Lagunillas)	density-elementary analysis	6.2
Royal Spectra	density - H/C approximated from x-ray L_a values[2]	2.5
Statex B	density - H/C approximated from x-ray L_a values[2]	2.3

Part C

Density, Elementary Analysis, and Values of C/R for Three Asphaltenes Prepared from Crude Oils of Widely Different Geographic Origin

Field	Location	Helium Density ρ	Elementary Analysis Per Cent C	H	O*	N	S	C/R Calculated by Means of Equation (6)	(25)
Lagunillas	Western Venezuela	1.158	84.2	7.9	1.6	2.0	4.8	3.46	6.24
Wafra	Neutral Territory (Middle East)	1.164	81.8	8.1	1.5	1.0	7.8	3.14	5.90
Baxterville	Mississippi U.S.A.	1.172	84.5	7.4	1.7	0.8	5.6	3.62	6.19

1 Measurements made in this laboratory.
2 Taken from the work of Kuroda, H., J. Colloid Sci., 12, 496 (1957).
3 Calculated assuming all the carbons are contained in a condensed aromatic sheet.

* Direct determinations

Table II
Calculation of R for
Compounds Consisting of Condensed Aromatic Ring Systems

Compound	Formula	Molecular Weight M	Density ρ	K_M	Rings per Molecule, R: Theoretical From Formula	Rings per Molecule, R: Calculated by Equation (24)
naphthalene	$C_{10}H_8$	128	1.152[1]	12.7	2	1.4
anthracene	$C_{14}H_{10}$	178	1.25[1]	27.2	3	3.0
fluorene	$C_{13}H_{10}$	166	1.203[2]	21.7	3*	2.4
triphenylene	$C_{18}H_{12}$	228	1.302[1]	40.3	4	4.4
chrysene	$C_{18}H_{12}$	228	1.274[1]	36.2	4	4.0
perylene	$C_{20}H_{12}$	252	1.35[1]	48.5	5	5.3
anthanthrene	$C_{22}H_{12}$	276	1.39[3]	56.4	6	6.2
coronene	$C_{24}H_{12}$	300	1.377[4]	57.0	7	6.3
ovalene	$C_{32}H_{14}$	398	1.477[5]	90.7	10	10.0
circumanthracene	$C_{40}H_{16}$	496	1.52[6]	119	13	13.1

* Contains one five-membered ring.

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6. E. Clar, et al., J. Chem. Soc., 1956, 3876.

Table III
Calculation of R for
Compounds of Varying Structure and Elementary Composition

Compound	Formula	Molecular Weight M	Density ρ	Rings per Molecule: Theoretical From Formula	Rings per Molecule: Calculated by Equation (24)
d-tartaric acid	$C_4H_8O_6$	150	1.759[1]	0	0
hexachloroethane	C_2Cl_6	237	2.09[2]	0	0
borneol	$C_{10}H_{18}O$	154	1.011[2]	1	0.7
p-hydroxybenzoic acid	$C_7H_6O_3$	138	1.46[2]	1	0.5
anthraquinone	$C_{14}H_8O_2$	208	1.43[2]	3	2.8
α-naphthylphenylmethane	$C_{17}H_{14}$	218	1.165[3]	3	2.7
papaverine	$C_{20}H_{21}NO_4$	339	1.337[4]	3	2.8
rosin	$C_{20}H_{29}O_2$	302	1.095[5]	3	2.5
laudanine	$C_{20}H_{25}NO_4$	243	1.26[2]	3	2.1
α-progesterone	$C_{21}H_{30}O_2$	314	1.166[2]	4	4.2
20-methylcholanthrene	$C_{21}H_{16}$	268	1.28[2]	5	4.2
strychnine	$C_{21}H_{22}N_2O_2$	334	1.359[4]	5	4.5

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2. "The Merck Index of Chemicals and Drugs," 6th Ed., Merck and Co., Inc., Rahway, New Jersey, 1952.
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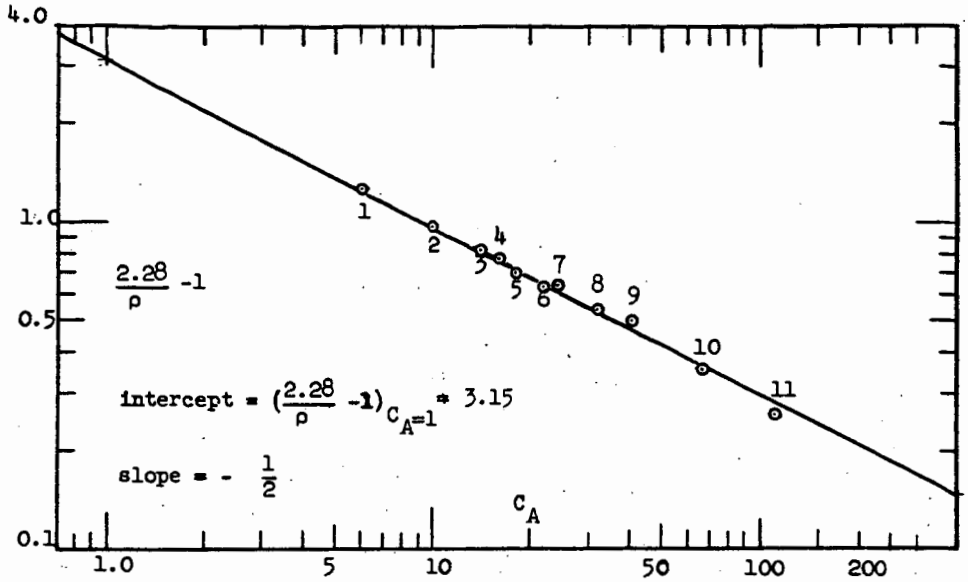

Figure 1

Relation of Density to Aromatic Carbon Number

(1) Benzene (2) Naphthalene (3) Anthracene (4) Pyrene
(5) Triphenylene (6) Anthanthrene (7) Coronene (8) Ovalene
(9) Circumanthracene (10) Royal Spectra (11) Statex B

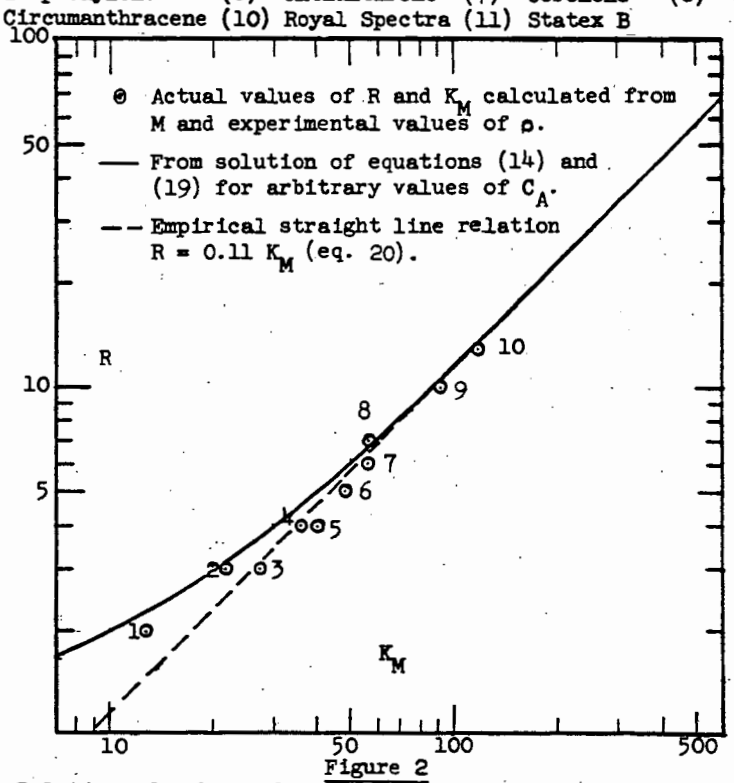

Figure 2

Relation of Molar Volume Contraction and Ring Number

(1) Naphthalene (2) Anthracene (3) Fluorene
(4) Chrysene (5) Triphenylene (6) Perylene
(7) Anthanthrene (8) Coronene (9) Ovalene
(10) Circumanthracene