NOMOGRAPHIC DETERMINATION OF THE MOLECULAR MASS OF PARAFFIN WAXES

By

I. SZERGÉNYI and J. SIMON*

Department of Chemical Technology, Technical University, Budapest

Received July 10, 1975
Presented by Doz. Dr. I. SZEBÉNYI

In addition to generally used data (melting point, oil content etc.), molecular mass data are being frequently utilized for characterizing paraffin waxes. Knowledge of the molecular mass is, on the one hand, indispensable for some special grading procedures ndM group composition test (Gross and Grodde rating), and on the other hand, yields in itself valuable information on paraffin waxes [1 to 4].

Paraffin waxes are mixtures of various hydrocarbons. Their molecular mass is an average value, defined by the nature and relative percentage of the individual constituents.

Owing to practical reasons, the application of the numerous well-known methods for molecular mass determination to paraffin waxes is rather cumbersome. Therefore, based on the experimental data of FERRIS and co-workers [5], MILLS, HIRSCHLER and KURTZ [6] developed, as early as 1946, an empirical procedure specifically for the determination of the molecular mass of paraffin waxes, having the advantage of being simpler and faster than any other method. The only experimental data required are the melting point and the refractive index of the paraffin wax.

The objective of our work was to improve the nomogram constructed by MILLS and co-workers, and to check the accuracy of the results obtainable with the improved nomogram.

Nomogram for determining the molecular mass of paraffins

The original nomogram published by MILLS and co-workers [6], representing the relationship between the molecular mass, the refractive index at 80 °C and the melting point paraffin waxes is reproduced in Fig. 1.

The nomogram is to be used as follows: a perpendicular line is drawn to the axis of abscissae at the point corresponding to the measured refractive

---

* Hungarian Petroleum and Natural Gas Research Institute.

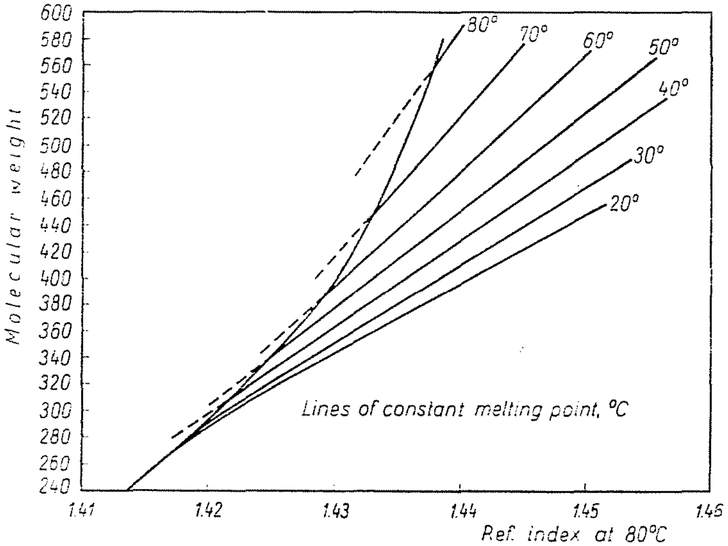

Fig. 1. Original nomogram by Mills, Hirschler and Kurtz for the determination of the molecular mass of paraffin waxes

index. Its point of intersection with the appropriate melting point line, projected onto the axis of ordinates, directly yields the molecular mass of the specimen. The use of the original nomogram is somewhat inconvenient, owing to the fact that it had been constructed for paraffins with melting points of 20, 30, 40, 50, 60, 70, 80 and 90 °C only. Since, however, there exists a regularity in the course of the empirical curves constructed by Mills, it should be possible to obtain a more detailed nomogram by graphical interpolation. We effected this by constructing the melting point lines at intervals of 1 °C. Our detailed nomogram is shown in Fig. 2.

Accuracy of molecular mass values obtained by means of the nomogram

Mills and co-workers reported that they checked the accuracy of their method experimentally. The average difference between the results obtained with the nomogram and with the control method was ± 5%. However, due to the mentioned difficulties in determining the molecular mass of paraffin waxes, the latter results also involved the risk of being inaccurate. Hence it is difficult to decide whether the results obtained by the Mills method or by the control method were truer. We therefore also investigated the accuracy of the molecular mass values obtained with our more detailed nomogram. The samples investigated included tabular commercial macrocrystalline grades (samples 1 and 2), macrocrystalline paraffin waxes with

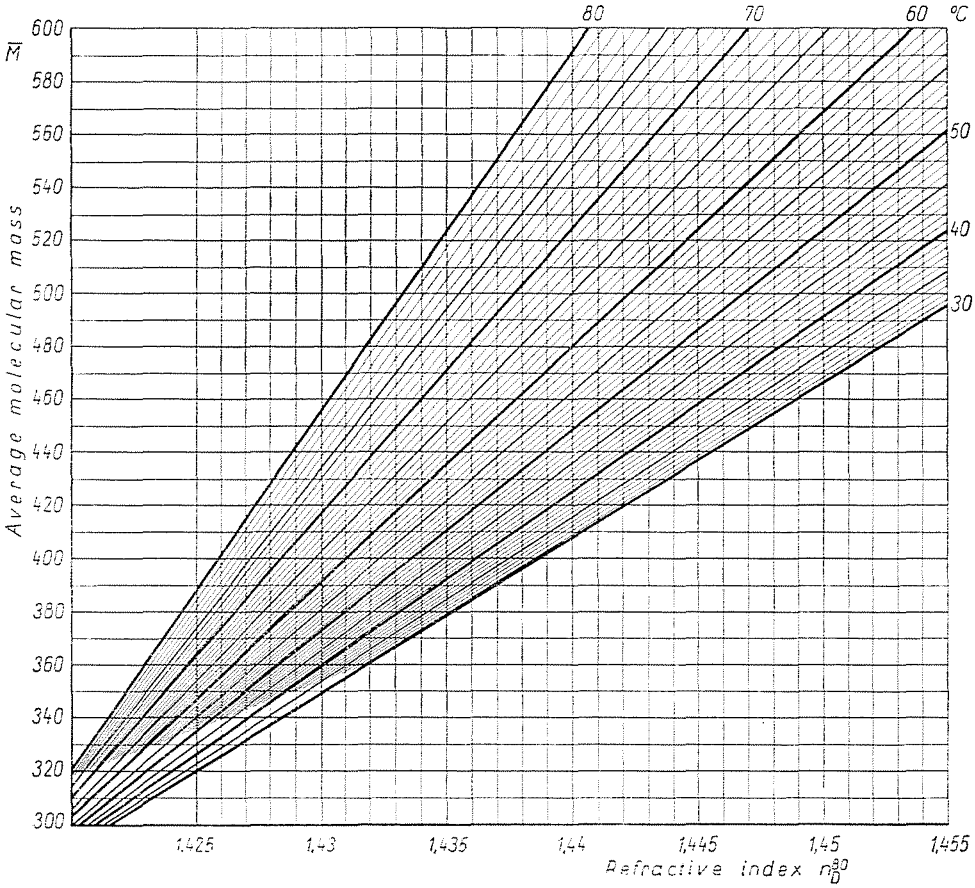

Fig. 2. Nomogram representing the relationship between the molecular mass, melting point and refractive index for paraffins

enriched *n*-alkane content* (samples 3 and 4), and the microcrystalline paraffin wax ceresine (sample 5). Melting point and refractive index data, as well the molecular mass as read from these data in the nomogram shown in Fig. 2 are summarized in Table 1.

The control method used for samples 1 to 4 was essentially the same, while a different method was applied for sample 5. With samples 1 to 4, we determined the distribution by carbon atom number of the individual hydrocarbons in the paraffin wax. The sum of the products of molar ratio and molecular mass of the individual constituents yields the average molecular mass of the paraffin wax. Thermoosmometry was used to determine the molecular mass of sample 5. The results obtained were as follows:

---

* Enrichment was carried out by using molecular sieves [7].

Table 1

Characteristics of the samples

Characteristic	Sample				
	No. 1	No. 2	No. 3	No. 4	No. 5
Refractive index n_D^{80}	1.4265	1.4295	1.4256	1.4283	1.4420
Melting point, °C	52.5	58.0	52.5	61.0	75
Molecular mass	350	388	343	381	575

Macrocrystalline paraffin waxes. The distribution by carbon atom number in samples 1 to 4 was determined by gas chromatography, using a PYE 104 gas chromatograph fitted with a flame ionization detector. The chromatograms are presented in Figs 3 to 6. We also determined the distribution of the constituents in sample 4 by mass spectrometry [7]. The data are summarized in Table 2.

These methods allow only a limited accuracy of measurement for individual constituents. However, we assumed that in our case, i.e. in a multiconstituent system, inaccuracies relative to individual constituents will compensate each other. The correctness of this assumption was confirmed by the fact that the molecular mass values obtained for sample 3 by gas

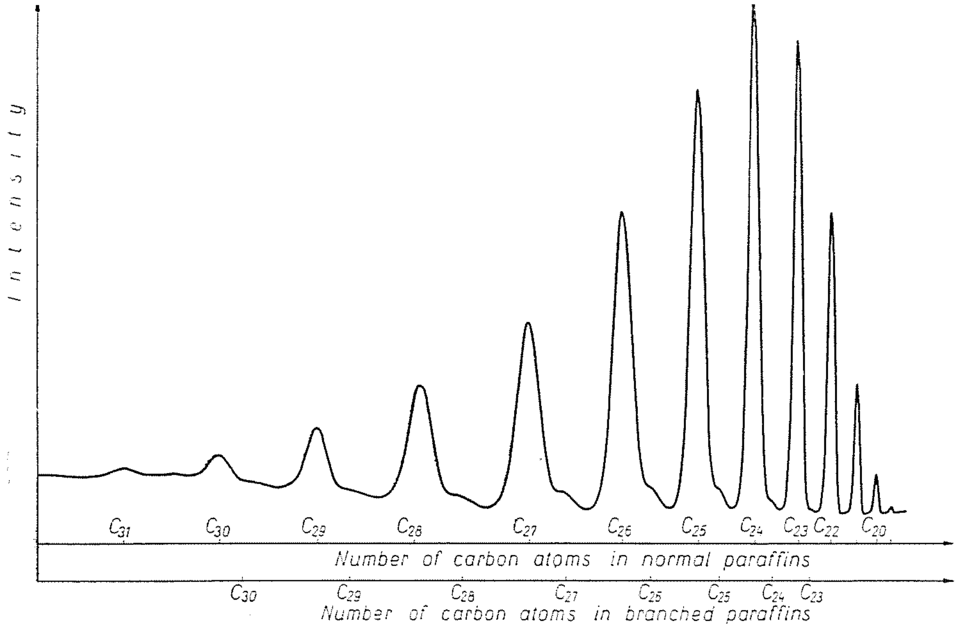

Fig. 3. Gas chromatogram of sample No. 1

Table 2

Distribution of hydrocarbons by carbon atom number in mycrocrystalline paraffin vawes

Number of carbon atoms	Molecular mass M	Per cent by weight in sample				
		No. 1	No. 2	No. 3		No. 4
				a	b	
19	268.53	0.14	0.23	0.25	0.6	0.27
20	282.57	0.60	0.69	0.76	1.4	0.54
21	296.60	2.23	1.38	2.03	2.9	0.80
22	310.63	5.36	1.83	5.57	7.4	1.07
23	324.66	12.39	2.75	11.14	15.0	1.61
24	338.69	16.52	4.59	16.71	19.8	2.41
25	352.72	18.01	7.80	18.99	18.2	5.36
26	366.75	17.22	14.22	16.20	15.8	10.19
27	380.78	12.76	16.97	12.15	10.5	13.67
28	394.81	8.63	17.20	9.11	5.5	19.30
29	408.84	4.32	14.68	4.30	2.1	17.43
30	422.85	1.37	8.72	2.28	0.8	14.75
31	436.90	0.45	5.50	0.51	—	7.51
32	450.93	—	3.44	—	—	4.29
33	464.96	—	—	—	—	0.80
Total		100.0	100.0	100.0	100.0	100.0

Table 3

Comparison of molecular mass values obtained nomographically and experimentally

	Sample					
	No. 1	No. 2	No. 3		No. 4	No. 5
			a	b		
Molecular mass nomographical	350	388	343	343	381	575
Molecular mass experimental	353*	383*	355*	346**	392*	579***
Difference, %	0.8	1.3	3.4	0.9	2.9	0.7

* Calculated from gas chromatography results by Eq. (1).
** Calculated from mass spectrometry results by Eq. (1).
*** Thermoosmometic experimental value.

chromatography (a) and mass spectrometry (b) were in good agreement, although the percentages by weight of the individual constituents obtained by the two methods differ (cf. columns "a" and "b" for sample 3 in Tables 2 and 3).

The relative amounts of the individual constituents are obtained in percentage by weight rather than in molar fractions by both gas chromatography and mass spectrometry. The average molecular mass $\overline{M}$ was calculated from these data by the following equation [8]:

$$\overline{M} = \frac{1}{\sum_{i=m}^{n} \frac{r_i}{M_i}} \tag{1}$$

where M_1 is the molecular mass of the paraffin constituent, r_i the cross corresponding weight fraction, m and n the lower and upper limit of the carbon atom number in the given paraffin fraction.

Molecular masses and distribution by carbon atom number of the individual constituents are listed in Table 2.

The average molecular masses obtained by Eq. (1) and the differences as compared with the molecular mass values obtained by the nomogram are presented in Table 3, indicating that the differences are inferior to 4%.

Microcrystalline paraffin wax. The molecular mass of sample 5 was measured by thermoosmometry, because neither gas chromatography nor mass spectrometry proved successful for the quantitative determination of the distribution of ceresine constituents.

The principle of thermoosmometry consists in the followings: a drop of a solution and a drop of pure solvent are placed, at constant temperature, into an atmosphere saturated with the vapour of the solvent. Since the vapour pressure of the solution is lower than that of the pure solvent, condensation of the solvent vapour onto the solution drop will start. As a result of condensation, the temperature of the solution drop will increase. The temperature difference between the solution drop and the solvent drop is determined by a suitable instrument. The temperature difference is proportional to the molarity of the solution. Hence, if a calibration curve is at disposal, the molecular mass of the dissolved substance can be calculated [9, 10].

Using a Kramer vapour pressure osmometer, we prepared a calibration curve with different concentrations of the model substance squalane [11, 12] and subsequently determined the thermal effect with a ceresine solution of known concentration (in g/l). From the molarity corresponding to the obtained thermal effect on the calibration curve, the average molecular weight of the sample was calculated as

$\overline{M} = \frac{\text{concentration of sample (g/l)}}{\text{found molarity}} = 579$ [13] in agreement with the nomographically determined value at an accuracy of 0.7% (Table 3).

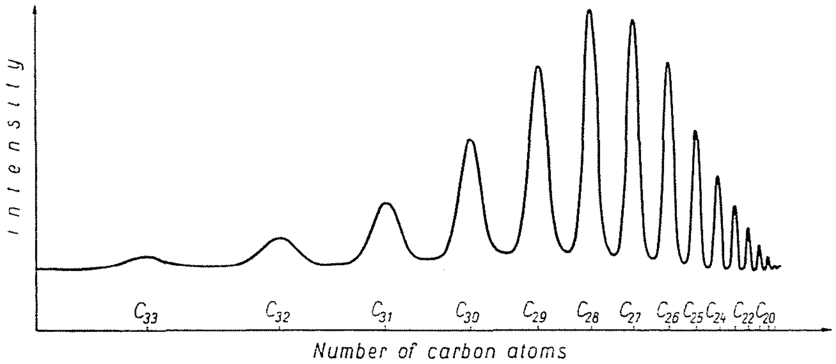

Fig. 4. Gas chromatogram of sample No. 2

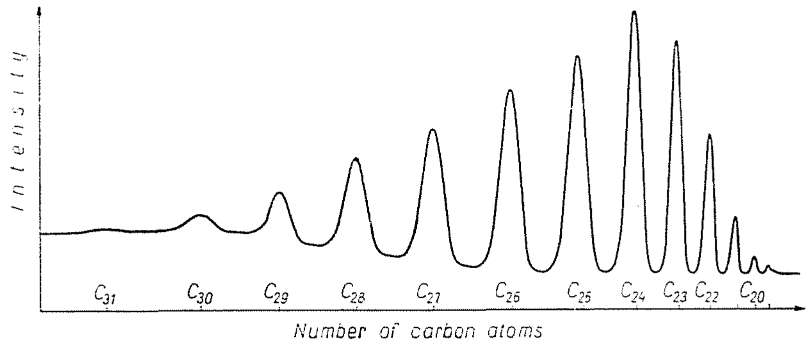

Fig. 5. Gas chromatogram of sample No. 3 (= normal paraffin fraction of sample No. 1)

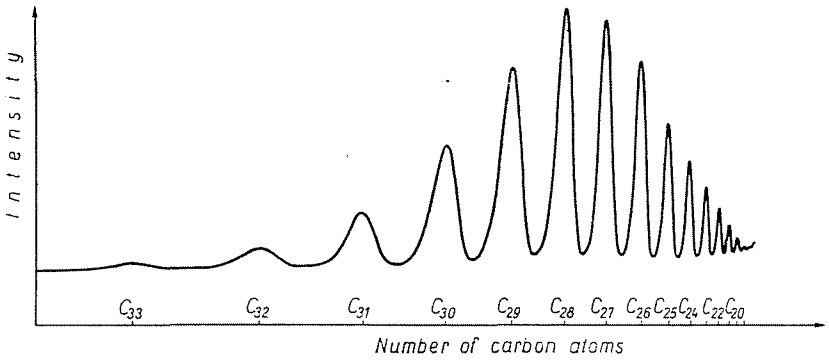

Fig. 6. Gas chromatogram of sample No. 4 (= normal paraffin fraction of sample No. 2)

Acknowledgements

The authors wish to express their gratitude to Professor Dr. L. VAJTA, Department of Chemical Technology, to Assistant Professor Dr. I. SZEBÉNYI, Head of the Department of Chemical Technology, Technical University Budapest, to Dr. R. CSIKÓS, Director of the Hungarian Petroleum and Natural Gas Research Institute, for their valuable help, and to Dr. I. BOZSÓ, senior research worker at the Hungarian Petroleum and Natural Gas Research Institute, for carrying out the thermoosmometric measurements.

Summary

Improvement of a nomographic procedure developed earlier allowed to determine the molecular mass of macro- and microcrystalline paraffin waxes at an accuracy of 4%. The only experimental data required for the procedure are the refractive index and the melting point of the paraffin wax.

References

1. VAN NES,—VAN WESTEN: Aspects of the Composition of Mineral Oils. Elsevier Publ. Co., 1951, p. 344
2. GROSS, H.—GRODDE, K.: Öl u. Kohlen, **1942**, 419
3. SZERGÉNYI, I.: Bányászati és Kohászati Lapok, Kőolaj és Földgáz, **6**, 1976 (1970)
4. FREUND, M.—CSIKÓS, R.—KESZTHELYI, S.—MÓZES, GY.: Kőolajparaffinok. Műszaki Könyvkiadó, Budapest 1973
5. FERRIS, S.—COWLES, H.—HENDERSON, L.: Ind. Eng. Chem., **23**, 681 (1931)
6. MILLS, W.—HIRSCHLER, A.—KURTZ, S.: Ind. Eng. Chem., **38**, 442 (1946)
7. SZERGÉNYI, I.—TAMÁS, J.—SOMOGYINÉ, H. Zs.: Magy. Kém. Foly., **75**, 347 (1969)
8. ERDEY-GRÚZ, T.—SCHAY, G.: Elméleti fizikai kémia, II. k. Tankönyvkiadó, Budapest, p. 11. (1964)
9. SIMON, W.—CLERC, I.—DÜHNER, R.: Microchem. J., **10**, 495 (1966)
10. NEUMAYER, I.: Anal. Chim. Acta, **20**, 519 (1959)
11. BURGER, J. P.: U. S. Atomic Energy Comm. S. C. D. C.—64, 380, 21 (1964)
12. ASTM D 2503—66T
13. BOZSÓ, I.: MÁFKI Research Report, J—55/1968

Dr. István SZERGÉNYI }
Dr. Jolán SIMON } H-1521 Budapest