PHYSICAL SCIENCES

THE DETERMINATION OF MOLECULAR WEIGHTS OF NON-VOLATILE PETROLEUM OILS[1]

JOHN M DEVINE[2]

INTRODUCTION

THE IMPORTANCE of determination of molecular weights or, more truly, of average molecular weights has not been recognized as extensively in investigative work on petroleum as is justified. This has been due partly to inability to obtain results in which the investigator could place full confidence. Mabery,[3] in studying the lighter lubricants from Appalachian crude oils, attained fair success with the ebullioscopic method, using benzol as a solvent. However, he found the cryoscopic method, using stearic acid as a solvent, more satisfactory, especially with the heavier types of oils. Even with the latter method he noted occasional inconsistencies, supposedly due to irregularity in the initial separation of crystals. Seaton and Sawyer,[4] in their study of paints and varnishes, tried both the cryoscopic and ebullioscopic methods with benzol and chloroform as the respective solvents, but reported no success. They later used stearic acid as a solvent in a cryoscopic apparatus of essentially the Beckmann type but with the exception that an electrical resistance wire was wound around the upper portion of the inner tube to prevent crystallization of the solvent. Seaton and Sawyer obtained satisfactory results by this method, although they observed that the freezing point of the stearic acid could not be determined within 0.01° C. R. E. Wilson and E. P. Wylde[5] used benzol as a solvent in the cryoscopic method and reported excellent results with various gas-absorbent and light lubricating oils having molecular weights varying from 160 to 260. With oils of molecular weight above 400, the results obtained were not dependable. Carpenter[6] applied the ebullioscopic method to the determination of molecular weights of paraffin wax, using benzol, chloroform, and carbon tetrachloride as solvents. The results obtained apparently were satisfactory. He was unsuccessful with cryoscopic methods. Rhodes, Mason, and Sutton,[7] in their study of crystalline wax, determined molecular weights by means of the cryoscopic method, using naphthalene as a solvent. No data were submitted as to the accuracy of this method. In his work on molecular weights, Rast[8] described a microcryoscopic method with camphor as a solvent.

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[1]Read by permission of the Director of the U. S. Bureau of Mines before the Oklahoma Academy of Science, Stillwater, Okla., Nov. 30, 1928.

[2]Assistant Organic Chemist, U. S. Bureau of Mines, Petroleum Experiment Station, Bartlesville, Oklahoma.

[3]Ind. Eng. Chem. 15, 1234, (1923).

[4]J. Ind. Eng. Chem. 8, 490, (1916).

[5]Ind. Eng. Chem. 15, 802, (1923).

[6]J. Inst. Petroleum Tech. 56,, 288-315, (1926).

[7]Ind. Eng. Chem. 19, 935, (1927).

[8]Ber. 55, 1051, (1922).

SCOPE

This paper gives the results obtained in the determinations of molecular weights of petroleum oils, as well as of pure substances, by both cryoscopic and ebbullioscopic methods employing various solvents.

APPARATUS

The boiling-point determinations were made by means of the Menzies-Wright apparatus with differential thermometer.[9] It is believed that the use of this apparatus eliminates many of the errors inherent in the older types of boiling-point apparatus—namely, super-heating, uncertainty as to actual concentration of the solute, and errors due to fluctuation of barometric pressure.

The Menzies-Wright apparatus (fig. 1) consists of a boiling tube (A) whose narrowed upper portion serves as a condenser tube. A glass cylinder (B), open above and below and of a diameter slightly less than that of the boiling tube, is fixed concentrically within the latter. Within (B) is

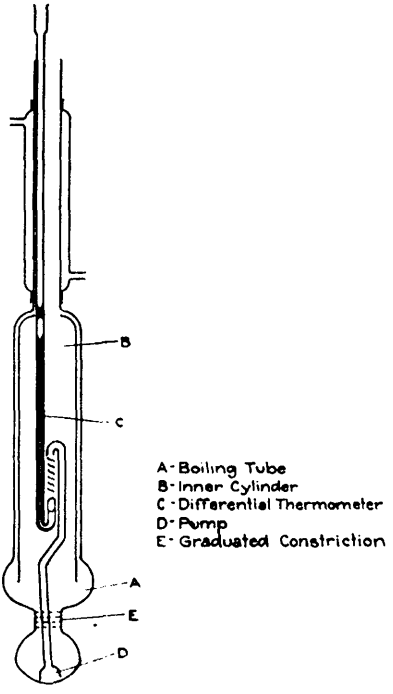

Fig. 1- Menzies-Wright Apparatus

supported the differential thermometer (C), on the lower bulb of which the pump (D) hangs loosely. The constriction (E) at the lower end of the boiling tube is graduated in cubic centimeters. Heating is by means of an ordinary Bunsen burner with a metal shield. When boiling begins, portions of the liquid are carried up through the pump and discharged in a

[9] J. Am. Chem. Soc. 43, 2314, (1921).

thin film over the lower bulb of the thermometer, which thus attains the temperature of the boiling solution. The upper bulb attains the temperature of the vapor of the boiling solvent. The thermometer registers the difference between these two temperatures.

In operation, the boiling tube is clamped vertically, the bulb of the boiling tube is filled with solvent to the lower graduation mark, and the condenser water is turned on. Heat is applied, and the boiling point of the solvent is determined to 0.1 degree by means of a high-grade mercury thermometer. The working volume of the solvent is then determined by removing the burner and immersing the bulb of the tube in cold water. When boiling ceases the volume of solvent is read at the graduated constriction before any drainage takes place. The differential thermometer and pump are inserted, and boiling is resumed. When equilibrium is reached, readings of the stem and the lower bulb of the differential thermometer are taken, and the difference between the two is recorded as the zero reading. Sufficient sample is added to give an approximate rise of .0.1 degree in the boiling point of the solvent, and the readings on the thermometer are again taken. This difference minus the zero reading gives a differential in millimeters which may be transposed to temperature difference by means of suitable tables.

EXPERIMENTAL

Recently it became necessary to determine the molecular weight of a brominated oil prepared from Inglewood, California, crude. Previous work in the laboratories of the Petroleum Experiment Station of the Bureau of Mines on the average molecular weights of petroleum has always been unsatisfactory, as the results on the same sample with different solvents varied occasionally as much as 50 percent. Therefore, before attempting to determine the molecular weight of the brominated oil, it was decided to make a number of preliminary runs with a solute of known molecular weight.

Diphenyl ether, purchased from the Eastman Kodak Co., was selected for the runs because of its high boiling point, liquid condition at room temperature, and the ease with which it can be purified. The following determinations were made by the Menzies-Wright method, using carbon tetrachloride as solvent. The results were:

Run No. 1. 159, 157.
Run No. 2. 159, 179, 159, 158.

With the exception of the second value in run No. 2, the agreement of the determinations was considered satisfactory. However, with the exception of the one named, all results were low, as the true molecular weight of diphenyl ether is 170. The bulk of the diphenyl ether was accordingly recrystallized once and the determinations were repeated. The results were: 171, 173, 178, 171, 169.

With benzol as a solvent, the diphenyl ether showed the following molecular weights: 172, 165, 163, 167.

In order to check further the accuracy of the method, pure naphthalene was used as solute and carbon tetrachloride as solvent. The results were: 132, 129, 126, 123, and 123; average 127. The true molecular weight of naphthalene is 128.

These results indicate that the method is capable of giving a reasonable degree of accuracy with pure substances.

For the work on petroleum, a special oil was prepared by distilling topped Inglewood crude at an absolute pressure below 2 mm. of mercury. All fractions so obtained were combined into a single sample. The results of molecular weight determinations on this sample are here tabulated:

MENZIES-WRIGHT METHOD USING BENZOL AS SOLVENT

Run No. 1		Run No. 2		Run No. 3		Run No. 4	
M.W.	Conc.*	M.W.	Conc.*	M.W.	Conc.*	M.W.	Conc.*
303	14	345	12	321	11	314	11
314	27	329	23	325	24	326	23
330	41	348	35	330	35	335	34
		345	47			340	46

*Concentration in mg. of solute per gm. of solvent.

With the exception of Run No. 2 the molecular weights increased progressively with increasing concentration of solute (fig. 2).

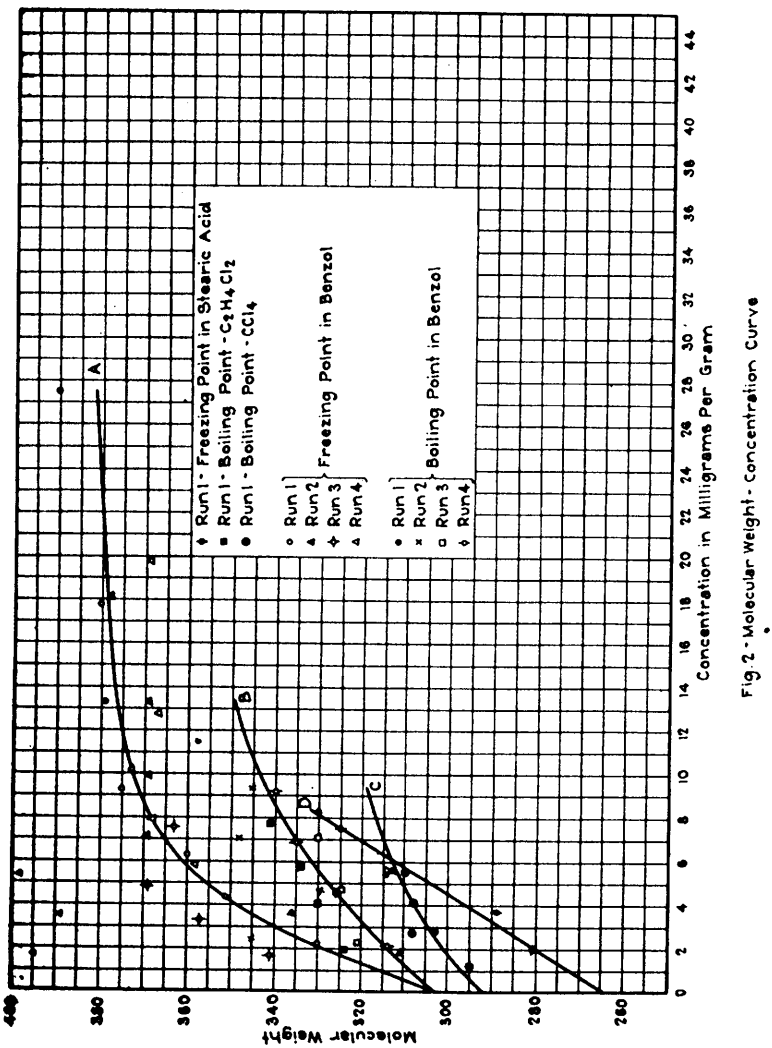

Fig. 2 - Molecular Weight - Concentration Curve

The following runs were made with other solvents.

MENZIES-WRIGHT METHOD USING CARBON TETRACHLORIDE AS SOLVENT

M.W.	Conc.*
295	6
308	13
308	21
310	28

MENZIES-WRIGHT METHOD USING ETHYLENE DICHLORIDE AS SOLVENT

M.W.	Conc.*
324	10
330	21
334	23
341	39

*Concentration in mg. of solute per gm. of solvent

In order to check the foregoing results against the cryoscopic method the following determinations were made on the same oil, using benzol as solvent. The ordinary Beckmann cryoscopic apparatus was employed in these determinations.

FREEZING POINT METHOD USING BENZOL AS SOLVENT

Run No. 1		Run No. 2		Run No. 3		Run No. 4	
M.W.	Conc.*	M.W.	Conc.*	M.W.	Conc.*	M.W.	Conc.*
330	11	395	9	341	8	311	9
351	22	389	18	357	17	336	18
360	32	398	27	369	24	358	29
375	47	369	36	363	38	358	39
379	66	369	49	370	49	373	51
380	89	369	66			367	64
390	138	378	90			369	99

*Concentration in mg. of solute per gm. of solvent.

Finally, the molecular weight of the distilled oil was determined in stearic acid (U.S.P.) which was dried at a temperature slightly above 100°C. The results were:

FREEZING POINT METHOD USING STEARIC ACID AS SOLVENT

M.W.	Conc.*
281	10
289	19
313	28
325	38

*Concentration in mg. of solute per gr. of solvent.

These results were distinctly lower than those previously obtained (see fig. 2). However, the trend of the results was similar to that already shown, that is, an increasing concentration of solute gave a progressively increasing value for the molecular weight.

An attempt was made to use both camphor and naphthalene as solvents in the cryoscopic method. The results were very erratic, doubtless due to the sublimation of a portion of the solvent and to subsequent indefinite increase in the concentration of the solute.

From the curves shown in Figure 2 it was evident that, in so far as the

present experimental work had gone, more concordant results were obtained when extrapolated values were used in preference to average values. Using this method, a molecular weight of 444 was obtained for the brominated oil previously mentioned (fig. 3). The percentage of bromine in the oil was known to be 37.12, which gave a calculated value of 431 for the molecular weight.

Thus the extrapolated value (444) was in much better agreement with

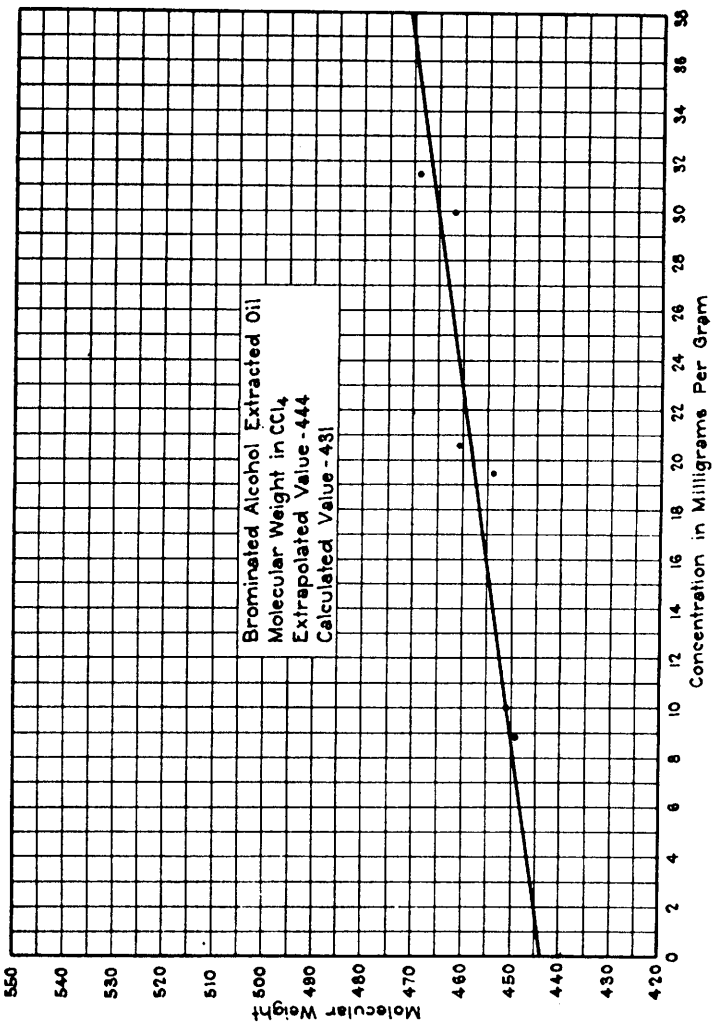

Fig. 3

the figure determined by analysis (431) than the value 458, which is the average of the individual determinations of the molecular weight of the brominated oil.

SUMMARY

Experimental results are given which show that the ebullioscopic and cryoscopic methods may give comparable results in the same solvent when the individual values are extrapolated; this is indicated by curves A and B in Figure 2, where A, the freezing point curve, is considerably removed from B, the boiling point curve, and yet the results at zero concentration as obtained by extrapolation are essentially the same. When the determinations are made in different solvents, even with the same method, extrapolation may fail to give results as concordant as those just referred to. For example, in ethylene dichloride the extrapolated value is approximately 5 percent higher than that obtained with benzol as a solvent, whereas in carbon tetrachloride, the corresponding value is approximately 5 percent lower. When stearic acid is employed as a solvent the results are decidedly lower, as shown by curve D.

At best, the status of molecular weight determination in relation to heavier petroleum oils is unsatisfactory and if these oils are considered to be isocolloidal in character it is easy to understand that the question of methods and technique is not the only obstacle in the way of successful solution of the problem.