SHORT COMMUNICATIONS

THE SPECTROPHOTOMETRIC ESTIMATION OF MOLECULAR WEIGHTS OF POLYETHYLENE GLYCOLS DISSOLVED IN BENZENE*

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In the course of other work the near infra-red spectra of six polyethylene glycols (PEG's) have been examined in benzene solution. The samples were gifts from the Shell Company and were used without further purification. " PEG's 200 and 300 " were viscous oils, " 800 " and " 1500 " were waxes, while

Table 1

SPECIFIC EXTINCTION COEFFICIENTS AT 7140 cm^{-1} FOR THE POLYETHYLENE GLYCOLS DISSOLVED IN BENZENE

Solute " PEG "	c (g/100 c.c.)	I	(Log $(1/T)/cl) \times 10^{-2}$
200	1·6024	0·585	2·88
300	2·3700	0·515	2·43
800	2·5736	0·638	1·52
1500	2·2080	0·782	1·14
4000	1·8764	0·840	0·76
6000	1·9286	0·870	0·63

Table 2

COMPARISON OF MOLECULAR WEIGHTS FOUND CHEMICALLY OR SPECTROPHOTOMETRICALLY

Solute " PEG "	M_{chem}	M_{sp}
200	190– 200	170± 10
300	285– 315	285± 15
800	760– 840	810± 40
1500	1430–1570	1530± 75
4000	3300–3600	3760±190
6000	6000–7500	5800±290

" 4000 " and " 6000 " were apparently crystalline solids. Their molecular weight distributions, determined by end-group analyses, were as listed in Table 2 (second column). For purposes of calculation the mid-points of these ranges have been taken as the molecular weights M of the respective polymers.

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The spectra were recorded, through the 6200–8300 cm^{-1} overtone region, on a Perkin-Elmer Spectracord, concentrations of the order 2 g/100 c.c. being used in a 5-cm cell.

Each solution showed a sharp strong absorption at 7140 cm^{-1}, which being unchanged by dilution, was attributed to intramolecular hydrogen bonding (cf. Badger 1957). Other characteristics of interest found in the spectra were broad weak bands at 6400–6800 cm^{-1} (possibly caused by polymeric associations of

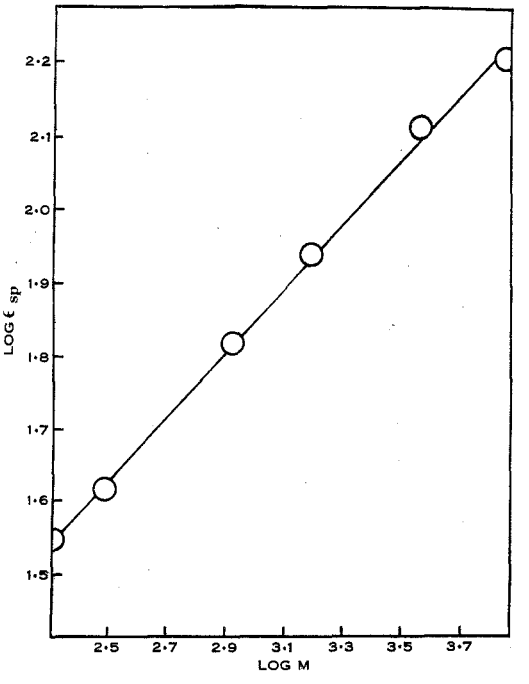

Fig. 1.—Log ε_{sp} *versus* log M.

the solute species), weak shoulders at 7040 cm^{-1}, and slight inflections at 7300 cm^{-1} (probably due to intermolecular hydrogen bonding and free-hydroxyl groups respectively (cf. Wulf and Liddel 1933, 1935, 1936; Mecke 1950; Holman and Edmondson 1956).

Quantitatively the transmission T at 7140 cm^{-1} can be related to the molecular weight of the solute. If specific extinction coefficients ε_{sp} be computed as log $(1/T) \div$ (concentration as g per 100 c.c.) $\times$ (cell length in cm), values such as those in Table 1 emerge. Log ε_{sp} is seen to have a rectilinear dependence upon log M (cf. Fig. 1); this may be expressed by

$$-\log \varepsilon_{sp} = 0 \cdot 45 \log M + 0 \cdot 51,$$

or

$$\log M = -0 \cdot 113 - 2 \cdot 22 \log \varepsilon_{sp}.$$

Table 2 illustrates the applicability of these equations to the substances under study. Agreement is satisfactory within the limits quoted, which are

based upon a 5 per cent. error in the extinction coefficient. No correction factors were applied to the measured transmissions; this was deliberate since the objective was to test a simple routine method for the determination of M. Even so, the technique is quicker and easier than the fairly involved chemical end-group analysis in current use (cf. Curme and Johnson 1952).

References

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