A new method to determine the shape of molecules of high polymers.

We have effected the determination of ultrasonic velocities by means of Hiedemann and coworkers' method, in various series of liquid compounds including high molecular weight substances.

At regards solid substances that cannot be easily melted determination was made in solution, admitting the relation:

$$u_x = \frac{1}{\frac{c}{u_1} + \frac{1-c}{u_2}} = \frac{1}{\left(\frac{x}{u_1 \rho_1} + \frac{1-x}{u_2 \rho_2}\right) \rho_x} ;$$

u_1, u_2, u_x are ultrasonic velocities in the two pure components and in the solution respectively: ρ_1, ρ_2, ρ_x are densities of the two pure components and of the solution respectively: c is volume concentration, x weight concentration of component 1 in the solution. We found the above relation proved valid exactly for solutions behaving like ideal solutions regarding the other physical properties (1). From the said formula knowing u_1 of the solvent, we derived u_2 of the other component of the solution.

Experimental velocities were compared to theoretical ones calculated with the Rama Rao formula (2) $R = \sqrt[3]{u}\,\frac{M}{\rho}$ (M = molecular weight; ρ = density; u = ultrasonic velocity), supposing R as summing partial R referring to the single chemical bounds composing the molecule (Lagemann and Corry (3)).

We give here the experimental values of u at 20°C and the ratio f between experimental and calculated velocities. The values of u regarding hydrocarbons containing less than ten atoms of carbon are derived from literature (4), all the other have been determined by us experimentally.

We found a relation between f and the branching of the molecules and we therefore call f « shape factor ».

As the above data clearly show non branches molecules and slightly frequently branched molecules present f equal or near the unit. Low molecular weight substances with branched molecules present f values only slightly below the unit. Such very small divergencies might be put down to the not strict applicability of Lagemann and Corry's values to branched compounds. A correction of Lagemann and Corry's values would not howerer be sufficient to explain the anomalies observed in the f values of high polymers.

Substance	u at 20°C ($m.sec^{-1}$)	$f = \frac{u_{exp.}}{u_{calc.}}$
n. Hexane	1126	1,00
n. Heptane	1154	0,97
n. Octane	1192	0,99
Hexadecene	1359	0,94
Parafine (m. p.) 60°C.)	1421	1,03
Fischer-parafine (m. p.) 90°C.)	1497	1,02
Polyethylene (m. w. ~ 20.000)	1702	0,94
2,2-Dimethylpentane	1080	0,95
3,3-Dimethylpentane	1129	0,91
2,2,3-Trimethylbutane	1101	0,90
Triisobuthylene	1237	0.90
Polyisobuthylene (m. w. ~ 3000)	1495	0.80
Polyisobuthylene (m. w. ~ 6000)	1520	0,80
Polyisobuthylene (m. w. ~ 15000)	1530	0.81
Polyisobuthylene (m. w. ~ 200000)	1588	0,82
Buthylrubber (polyisobutilene with 1-2% isoprene)	1558	0.76
Natural rubber	1620	0,91
Natural rubber 10' treated in mixing apparatus	1485	0,86
Ethylpentane	1169	0.92
Poly α-buthylene	1396	0,83
Poly α-buthylene with 21% butadiene	1418	0,73
Buna 32	1540	0.90
Hydrogenated Buna 32	1530	0.82
Toluene	1325	1,02
Ethylbenzene	1329	0,96
Styrene	1364	1,00
Polystyrene	1470	0,82
Methylacetate	1183	1,02
Methylpropionate	1173	0.98
Methylacrylate	1176	0,98
Methylpolyacrylate	1260	0,92
Isobuthylacetate	1178	0.98
Methylisobutirrate	1163	0.97
Methylmetacrylate	1218	0,96
Methylpolymetacrylate	1260	0,56
Ethyl ether	1006	1,02
Polyvinylisobuthylesther	962	0,62
Polyoxymethylene	1574	1,17
Polyethylenoxyd (m. p. 42°C.)	1602	1,01
Polyethylenoxyd (n. m.)	1619	1,02
Acetoacetoanilide	1655	1,00
Caprolactam	1610	1,06
Nylon 6-6	2000	1,35

High molecular weight polyoxymehtylenes and polycondensed substances like nylon 6-6 with certanly straight chained form show f greater than the unit. Common and Fischer parafines with molecular weight up to 3000 have f = ~ 1 whereas high polymers with frequently branched chains have f very much below the unit (0.91 natural rubber; 0,86 rubber for ten minutes treated in mixing apparatus; 0,90 Buna 32; 0,83 poly α-buthylene; 0,80-0,82 polyisobuthylene, hydrogenated Buna 32, polystyrene; 0,76 buthylrubber; 0,62 polyvinylisobuthylesther; 0,92 methylpolyacrylate; 0,56 methylpolymetacrylate).

The f shape factor depends not only upon the frequency of the branches of the molecules, but also upon the lenght of the branches.

The above data confirm that polymerisation of [illegible] butadiene in Buna does'nt take place in position 1-4.

From the above data we should assume that in compressibility of high molecular weight compounds in liquid state besides the free volume between the molecules and the configuration elasticities also an internal molecular elasticity is implied.

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