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LETTER TO THE EDITORS

ULTRASONIC VELOCITY IN MACROMOLECULAR SUBSTANCES

In a recent paper (1) we reported that the ratio of ultrasonic velocity to density in molten or dissolved macromolecular substances is related to the average molecular weight and the amount of branching in the molecule.

In a successive paper (2) we introduced the shape factor as the ratio of experimentally determined ultrasonic velocity to the calculated one, using Rama Rao's law (3) and utilizing Lagemann and Corry's values (4) of the ultrasonic bond velocity.

As these data clearly show, straight-chain and unbranched molecules present shape factors equal or near to unity, while branched molecules yield shape factor values below unity.

Further work on ultrasonic velocities in some low-molecular hydrocarbons, ethers, and esters discloses that divergencies between experimental and calculated values, as observed in high molecular compounds, exist also in low molecular substances, though the numerical values of the differences were considerably smaller in the latter. Therefore, Lagemann and Corry's ultrasonic bond velocities must be corrected in order to allow predictions of ultrasonic velocities in branched compounds.

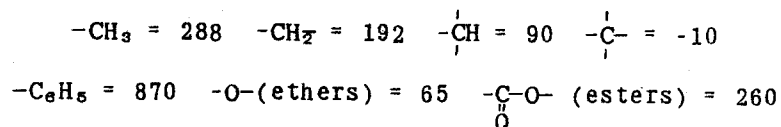
For this purpose we have found it more suitable to consider ultrasonic radical velocities rather than bond velocities, or Rama Rao's atomic velocities.

Thus we assume that the ultrasonic molecular velocity:

$$R = \frac{u^{1/3}}{\rho} M$$

(u = ultrasonic velocity, ρ = density, M = molecular weight) as the sum of all terms which correspond to each one of the radicals composing the molecule.

Form the measured ultrasonic velocities of the first liquid members of the series of hydrocarbons, ethers, and esters we have calculated the following values of ultrasonic radical velocities:



However we observed that lower values for radical velocities have to be used if the radicals are bound in side positions with respect

TABLE I

Substances	n_B/n_C	Branching type	Shape factors from bond velocities	Ultrasonic molecular velocities			Differences between experimental velocities and calculated velocities	
				Experimental	Calc. from bond velocities	Calc. from radical velocities	From bond velocities	From radical velocities
n-Hexane	0	-	1.007	1357	1354	1344	+3	+13
n-Heptane	0	-	0.979	1538	1548	1536	-10	+2
2-Methylhexane	0.167	CH ₃	0.970	1533	1548	1531	-15	+2
3-Methylhexane	0.167	CH ₃	0.949	1521	1548	1519	-27	+2
3-Ethylpentane	0.2	C ₂ H ₅	0.930	1513	1548	1511	-35	+2
2,2-Dimethylpentane	0.4	CH ₃	0.957	1526	1548	1526	-22	0
2,4-Dimethylpentane	0.4	CH ₃	0.956	1526	1548	1526	-22	0
2,3-Dimethylpentane	0.4	CH ₃	0.930	1511	1548	1514	-37	-3
3,3-Dimethylpentane	0.4	CH ₃	0.917	1505	1548	1502	-43	+3
2,2,3-Trimethylbutane	0.75	CH ₃	0.908	1500	1548	1509	-48	-9
n-Octane	0	-	0.969	1725	1743	1728	-18	-3
2,2,4-Trimethylpentane	0.6	CH ₃	0.933	1706	1743	1701	-37	+5

* n_B = number of branchings; n_C = number of carbon atoms in principal chain.

TABLE II

Substances ^a	n_B/n_C	Branch- ing type	Shape factors from bond ve- locities	Ultrasonic molecular velocities			Differences bet- ween experimental velocities and calculated velo- cities		
				Experi- mental	Calc. from bond ve- locities	Calc. from radical velocities	From bond ve- locities	From radical velocities	
Natural paraffin (m.p. 60°)	0	-	1.00	195	194	192	+ 1	+ 3	
Fischer paraffin (m.p. 90°)	-	-	1.02	196	194	192	+ 2	+ 4	
Polyethylene ($\eta_{sp}/c=8$; $c=0.1/0.2$)	0	-	1.01	195	194	192	+ 1	+ 3	
Polyethylene oxide ($\eta_{sp}/c=7$; $\eta_{sp}/c=0.1/0.5$)	0	-	1.03	458	454	449	+ 4	+ 9	
Nylon 6.6	0	-	1.00	2500	2500	2504	0	- 4	
Polyisobutylene ($\eta_{sp}/c=1$; $c=1$)	1	CH ₃	0.79	718	778	734	-60	-16	
Polyisobutylene ($\eta_{sp}/c=2$; $c=1$)	1	CH ₃	0.79	719	778	734	-59	-15	
Polyisobutylene ($\eta_{sp}/c=3.5$; $c=1$)	1	CH ₃	0.79	717	778	734	-61	-17	

TABLE II (continued)

Substances ^a	n_D/n_C	Branching type	Shape factors from bond velocities	Ultrasonic molecular velocities		Differences between experimental velocities and calculated velocities	
				Experimental	Calc. from bond velocities	From bond velocities	From radical velocities
Polyisobutylene ($\eta_{sp}/c=250$; $c=0.1/0.3$)	1	CH ₃	0.80	722	778	734	-56
Polyalphabutylene ($\eta_{sp}/c=1.2$; $c=1$)	0.5	C ₂ H ₅	0.82	729	778	742	-49
Hydrogenated Buna 32 ($\eta_{sp}/c=0.5$; $c=1/5$)	1 or 0.5	CH ₃ or C ₂ H ₅	0.82	729	778	734 or 742	-49
Butyl rubber ($\eta_{sp}/c=15$; $c=0.1/0.5$)	?	?	0.65	674	778	-	-105
Polystyrene ($\eta_{sp}/c=14$; $c=0.1/0.5$)	0.5	C ₆ H ₅	0.82	1090	1165	1152	-75
Polyvinyl isobutyl ether ($\eta_{sp}/c=50$; $c=0.1/0.3$)	0.5	$\begin{array}{c} \text{CH}_3 \\ \\ \text{O}-\text{CH}_3-\text{CH} \\ \\ \text{CH}_3 \end{array}$	0.78	1138	1232	1180	-102
Polymethyl methacrylate ($\eta_{sp}/c=15$; $c=0.1/0.3$)	1	$\begin{array}{c} \text{CH}_3 \\ \\ \text{OOCCH}_3 \end{array}$	0.63	887	1033	998	-146

^a m.p. = melting point; η_{sp} = specific viscosity; c = base moles in 1000 cc. of solvent.

to the main chain of the molecule. This lowering has been calculated to be -12 for $-\text{CH}_3$ radicals and -20 for $-\text{C}_2\text{H}_5$ radicals.

In Table I are reported data relating to ultrasonic velocities of low molecular hydrocarbons; the molecular velocities have been calculated introducing the lowering correction for $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$ branching. The table shows that if radical velocities are applied calculated ultrasonic molecular velocities and experimental ones are in better agreement than if bond velocities are applied.

Even for high molecular substances, reported in Table II, the differences between calculated ultrasonic molecular velocities and experimental ones are smaller if radical velocities are applied instead of bond velocities. However, these differences are still considerable, especially for the last substances in this table.

Since in the calculation of the molecular velocities we have only considered the branching-lowering correction for the $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$ radicals, the differences between the experimental and calculated values have to be ascribed to the branching-lowering due to $-\text{C}-\text{O}-$, $-\text{O}-\text{CH}_2-\underset{|}{\text{CH}}$ and $-\text{C}_6\text{H}_5$ radicals.

REFERENCES

1. G. Natta and M. Baccaredda, *J. Polymer Sci.*, **3**, 829 (1948).
2. G. Natta and M. Baccaredda, *Gaz. Chim. Ital.*, **79**, 364 (1949).
3. M. Rama Rao, *J. Chem. Phys.*, **9**, 682 (1942).
4. R. T. Lagemann and J. E. Corry, *ibid.*, **10**, 759 (1942).

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ERRATA

**Errata: SPECIFIC REFRACTIVITY-TEMPERATURE
DATA FOR POLYVINYL ACETATE
AND POLYBUTYL ACRYLATE**

(J. Polymer Sci., 4, 351-357, 1949)

**by Richard H. Wiley and G. M. Brauer
Venable Chemical Laboratories, University of North Carolina**

**Page 352, insert the following between lines 25 and 26:
sphere was derived by assuming that the forces by the atom
inside this**