ACOUSTIC RELAXATION AND PROPAGATION RATE OF HYPERSONIC WAVES IN LIQUIDS

G. G. Sukhotina, M.I. Shakhparonov

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Based on the experimental data which we have obtained as well as the data given in the literature, we shall calculate the parameters of acoustic relaxation for several organic liquids at 20°. /9*

The objects to be studied were selected in such a way as to determine the connection between the relaxation time and the lowest frequency of normal intramolecular oscillations ν_1. We performed measurements of hypersonic velocity V_r in decane, cyclohexane, decaline, ortho- and p-xylene, styrol, nitromethane, acetonitrile, tri- and tetrachlorethylene on the experimental equipment described in (Ref. 1).** These substances, which were marked "chemically pure", were studied after additional chemical purification and distillation. The values of the index of refraction n_D^m, density ρ_4^{20}, and boiling point (t_{min}) differed very little from those given in (Ref. 2) (see Table 1).

The figure presents examples of the microphotograms of the spectra which we studied of the Rayleigh line (λ = 4368 Å). The position of the Mandel'shtam-Brillouin components was determined on the basis of a method described by I. L. Fabeliiskiy (Ref. 3). The hypersonic velocity V_r and the hypersonic frequency f_r were calculated according to the following formulas

$$V_r = \frac{\Delta\nu \cdot \lambda \cdot c}{n\sqrt{2}} \qquad f_r = \frac{V_r n \sqrt{2}}{\lambda},$$

where Δ_ν is the displacement per cm^{-1} of the Mandel'shtam-Brillouin components with respect to the central component of the Rayleigh triplet, c -- speed of light, n -- liquid index of refraction, λ -- wavelength of incident radiation (4358 Å). The quantity V_r was determined within an accuracy of 2 - 4% (as a function of the ratio between the intensities of the central and marginal components of the Rayleigh triplet). It follows from Table 2 that the hypersonic velocity in cyclohexane C_6H_{12}, decaline $C_{10}H_{13}$, trichlorethylene C_2HCL***, tetrachlorethylene C_2Cl_4, and o-xylene C_1H_{10} exceeds the ultrasonic velocity

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* Numbers in the margin indicate pagination in the original foreign text.

** A. Normatov and O. Shakirov participated in measurements of the propagation rate and ultrasonic absorption in liquids.

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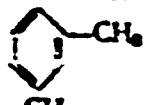
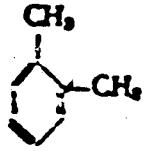
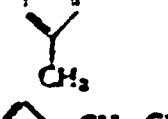
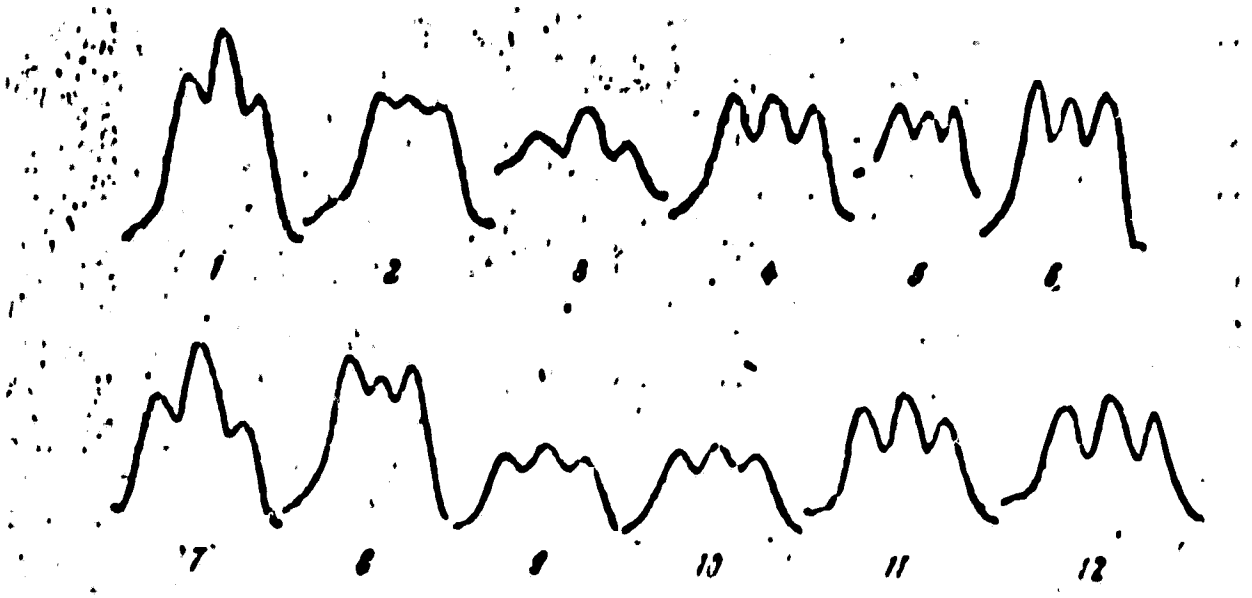
TABLE 1. CERTAIN PHYSICAL-CHEMICAL CHARACTERISTICS OF INDIVIDUAL LIQUIDS* /10

Substance	Formula	n_D^{20}	ρ_4^{20}, g/cm³	$\alpha_p \cdot 10^6$, deg^{-1}	C_p·2, cal/mole·deg	C_v·2, cal/mole·deg	C·2, cal/mole·deg	C_1^1 2, cal/mole·deg	V_s·3, m/sec	$\left(\frac{\alpha}{\rho}\right)_{\rho\to 0}^{10^{12}}$	$\left(\frac{\alpha_{ad}}{\rho}\right)_{\rho\to 0}^{10^{12}}$
Trans-decaline	 $C_{10}H_{18}$	1.4703	0.8965	86	54.5	43.4	31.6	1.89	1492	132	22.9
Decane		1.4120	0.7303	101.5	74.25	61.5	47.25	1.90	1255	54.4	16.9
Cyclohexane	 C_6H_{12}	1.4262	0.7788	120	36.7	26.60	16.85	1.82	1284	196	15.8
Hexane		1.3753	0.6594	135	46.2	36.2	25.80	1.87	1083	66	10.0
Toluene	 CH_3	1.4970	0.8666	110	37.23	27.2	16.4	1.81	1339	82.8	7.6
o-xylene	 CH_3 CH_3	1.5053	0.8802	97.3	43.8	33.75	23.45	1.86	1360	99	9.7
n-xylene	 CH_3 CH_3	1.4962	0.8606	101.1	43.10	32.95	21.90	1.89	1330	62	8.4
Styrene	 $CH=CH_2$	1.5469	0.9055	109	42.1	31.5	20.70	1.83	1407	55	8.2
Acetonitrile	CH_3CN	1.3442	0.7820	138	21.35	14.8	4.54	1.50	1309	58.3	5.4
Nitromethane	CH_3NO_2	1.3822	1.1372	119	25.3	17.6	5.75	1.28	1354	44	6.2
Tetrachlorethylene	C_2Cl_4	1.5060	1.6229	107.8	34.0	23.46	14.55	1.92	1058	233	12.2
Trichlorethylene	C_2HCl_3	1.4780	1.4661	119.3	29.3	19.73	11.25	1.97	1045	224	8.9

*a_p -- thermal expansion coefficient; c_1^1 -- oscillatory specific heat, corresponding to the smallest frequency of normal oscillations.

(1) -- degree^{-1}; (2) -- $\frac{\text{cal}}{\text{mole}}$; (3) -- $\frac{\text{m}}{\text{sec}}$



Microphotograms of the Fine Structure of the z-Component* of the Rayleigh Line of Light Scattering for the Liquids:
1 — C_6H_{12}; 2 — n-C_6H_{14}; 3 — $C_6H_5C_2H_5$; 4 — $C_6H_5CH_3$; 5 — o-$C_6H_4(CH_3)_2$; 6 — n-$C_6H_4(CH_3)_2$; 7 — $C_{10}H_{18}$; 8 — n-$C_{10}H_{22}$; 9 — C_2HCl_3; 10 — C_2Cl_4; 11 — CH_3CN; 12 — CH_3NO_2

by 4 - 5%, which may be caused by acoustic relaxation in the frequency region of $\sim 10^{10}$ cps. This conclusion is substantiated by calculations on the product of the sonic absorption coefficient α by the length of the sound wave Λ. /11 If it is assumed that there is no acoustic relaxation up to the frequencies $\sim 10^{10}$ cps, i.e., $\alpha/f^2 = \text{const}$, then for C_6H_{12}, $C_{10}H_{13}$, C_2HCl_3 and C_2Cl_4 $\alpha_* \lambda_r > 1$, and for C_3H_{10}, $\alpha_{or}\lambda_r \approx 1$; here $\alpha_{or} = (\alpha/f^2)_{f\to e} \cdot f_r^2$.

A fine structure is observed for the Rayleigh line. This is only possible when the condition $\alpha\lambda_r << 1$ is satisfied. Consequently, in actuality the absorption is less than the calculated absorption on the assumption that there is no dispersion. In other words, acoustic dispersion must occur. For styrene $\alpha_{or}\lambda_r = 0.61$ which, in all probability, is related to the great tendency of styrene towards spontaneous polymerization. The admixtures of polymer, which always occur in styrene, can sharply reduce the ultrasonic absorption. Therefore, the experimental value of $(\alpha/f^2)_{f\to o}$ for styrene, given in Table 1, is probably much lower than that which would be observed when there were absolutely no admixtures of polystyrene.

* Translator's note: Illegible in original foreign text.

TABLE 2. HYPERACOUSTIC PROPERTIES OF INDIVIDUAL LIQUIDS

Substance	[illegible] 1	[illegible] 1	[illegible] 2	[illegible] 3	[illegible] 4	[illegible]	[illegible]	[illegible]
Trans-decaline	5,2	1,4	1770	1457	1503	70,3	0,94	1,33
Decane	1,5	0,42	1565	1239	1282	36,7	0,33	0,38
Cyclohexane	6,7	2,8	1560	1340	1422	82,5	0,82	1,63
Hexane	2,0	0,57	1342	1076	1192	54,4	0,33	0,34
Toluene	3,1	1,2	1580	1358	1394	56,0	0,57	0,74
o-xylene	3,47	1,1	1675	1411	1420	60,0	0,67	0,89
n-xylene	2,3	0,77	1610	1337	1340	48,9	0,50	0,51
Styrene	2,0	0,69	1710	1425	1438	65,8	0,49	0,61
Acetonitrile	3,7	2,58	1355	1315	1349	28,0	0,25	0,44
Nitromethane	2,6	1,76	1450	1348	1389	26,2	0,26	0,36
Tetrachlorethylene	6,2	2,3	1300	1084	1156	137,3	0,69	1,34
Trichlorethylene	6,1	2,6	1550	1300	1187	109,0	0,67	1,27

(1) -- sec; (2) -- m/sec; (3) -- V_*, ex., m/sec; (4) -- V_*, theor., m/sec.

Based on the following formulas /12

$$V_\infty = V_0 \sqrt{\frac{(C_p - C')C_v}{(C_v - C')C_p}},$$

$$\frac{V_\infty^2 - V_r^2}{V_\infty^2 - V_0^2} = \frac{1}{1+(\omega\tau'')^2},$$

$$\tau'' = \frac{C_p \cdot C'}{C_v}\tau, \quad \bar{\tau} = \frac{2\pi' C_p \cdot C_v \cdot V_0}{\omega^2 (C_p - C_v) C'},$$

where V_0 -- speed of ultrasound, $\omega = 2\pi f$, C_p, C_v and C' -- molar specific heats for a constant pressure, volume, and total oscillatory specific heat, respectively, we may approximately determine the theoretical values of $V_{r,theor.}$ Table 2 presents the results of these calculations. It follows from the table (see columns 5 and 6) athat the divergence between $V_{r,theor.}$ and the experimental values $V_{r,exp}$ lies, as a rule, within the limits of possible experimental errors. Tetrachlorethylene, cyclohexane, and trichlorethylene represent exceptions to this. Everywhere we have $V_{r,theor.} > V_{r,exp}$, except for styrene. Certain divergences between experiment and theory may be explained by the fact that theory makes it possible only to determine the order of magnitude of τ.

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* Translator's note: Illegible in original foreign text.

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Division of Physical Chemistry