Ultrasonic Velocities in Trialkyl Borates

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The pulse-echo-overlap technique with a 10-MHz transducer was used to measure ultrasonic velocities in the following homologous series of trialkyl borates: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. The results obtained were correlated with various structural properties, and they were also employed to derive hitherto unreported molar heat capacities and absorption coefficients.

Systematic and extensive physicochemical investigations have been carried out in this laboratory for the following trialkyl borate homologues: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. These studies have yielded data on vapor pressures (*1*), densities and absolute viscosities (*2*), surface tensions (*3*), refractometric measurements (*4*), and thermal conductivities (*5*). The present investigation involves the measurement of ultrasonic velocities, u, and the determination of the structural property, R_a, deduced by Rao (*6*), and given by the equation

$$R_a = u^{1/3}V_m \quad (1)$$

where V_m is the molar volume. R_a has been shown not only to be of an additive and constitutive nature but also to be remarkably independent of temperature (*6*). Other such structural properties that can be determined from the works listed above include the Lorentz–Lorenz molar refraction (n, the refractive index, is for the sodium D line), R_D, and given by

$$R_D = V_m(n^2 - 1)/(n^2 + 2) \quad (2)$$

and Sugden's parachor, P, viz.

$$P = \gamma^{1/4}V_m \quad (3)$$

where γ is the surface tension. Correlations between R_a, R_D, and P have been obtained in this study. The ultrasonic velocity is related to the isothermal and adiabatic compressibilities, represented respectively by β_T and β_S, by the expressions

$$u^2 = k/\rho\beta_T = 1/\rho\beta_S \quad (4)$$

where k is the ratio of heat capacities, C_p/C_v, and ρ the density. The values of β_T for the straight-chain trialkyl borates previously reported (*7*) were calculated from the relationship deduced by McGowan (*8*), viz.

$$\beta_T\gamma^{3/2} = 1.33 \times 10^{-8} \text{ (cgs units)} \quad (5)$$

The well-known relationship

$$C_p - C_v = T\alpha^2/\rho\beta_T \quad (6)$$

where α is the coefficient of thermal expansion and T the absolute temperature, when combined with $C_v = C_p/k$, yields

$$C_p = T\alpha^2k/\{\rho\beta_T(k - 1)\} \quad (7)$$

which was used for the calculation of C_p.

In view of the availability of appropriate physical data for trialkyl borates, the determination of the so-called "classical" absorption coefficient, A, where $A = \alpha/f^2$ (α is the absorption and f the frequency), was undertaken. The coefficient is usually calculated from the Stokes–Kirchhoff equation (*9*), i.e.

$$A = \alpha/f^2 = (2\pi^2/\rho u^3)[4\eta/3 + (k - 1)\kappa/C_p] \quad (8)$$

Table I. Ultrasonic Velocities, Molar Volumes, and R_a

	t, °C	u, ms^{-1}	V_m, cm^3 mol^{-1}	R_a
trimethyl borate	30.7	1008.4	113.0	1133
triethyl borate	30.5	1004.5	171.5	1718
tripropyl borate	30.4	1094.8	221.5	2283
triisopropyl borate	30.0	963.7	233.0	2301
tributyl borate	30.4	1159.5	271.1	2848
triisobutyl borate	29.9	1102.5	275.5	2846

which assumes that the absorption may be ascribed to viscous and thermal effects alone (η is the viscosity and κ the thermal conductivity). Because of the complexities associated with the liquid state (particularly for polyatomic molecules), as reflected in the light of rather anomalous relaxation and scattering phenomena with regard to sound propagation, it is not surprising that values of A calculated from eq 8 are often appreciably lower than experimental observations. Nonetheless, estimates of A for trialkyl borates have not hitherto been reported, and thus the values given in this study may have some structural significance.

Experimental Section

The as-received borate samples were purified, assayed, and stored in the manner described previously (*1*). Ultrasonic velocities were measured by the pulse-echo-overlap technique (ref *9*, pp 97–9), with a 10-MHz transducer. The error in these observations is estimated to be ±0.1 ms^{-1}. Temperatures were read to ±0.1 °C.

Results and Discussion

Table I gives all information needed for the calculation of R_a from eq 1 (molar volumes were determined from data in ref *2*).

Among the numerous studies that have demonstrated the structural character of R_a, one of them (*10*) deduced the values 95.2 and 34.5 for the contributions of the CH and CO bonds, respectively. The use of these figures, along with the R_a's in Table I, yields the value 59.0 ± 1.6 as the effective contribution of a single BO bond to the trialkyl borate structure. This work also showed the functional relationship between R_a and several other structural properties (*10*). Another study (*11*) used the following expression for the estimation of u, the ultrasonic velocity

$$u = (x/V_m)^3 \quad (9)$$

where x represents a structural parameter somewhat similar to R_a in that it is made up of various group and constitutive contributions (a comprehensive table of such contributions is given in the article). Use of the figure 1850 for compounds with a basic methane structure, 872 for each additional CH_2 or CH_3 group, and 273 for O yields the value 951 ± 5 for the contribution of elemental boron to the structure factor x (following

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Table II. Experimental and Derived Data Involving Heat Capacities

	$10^4\beta_T$, atm^{-1}	$10^4\beta_S$, atm^{-1}	$10^3\alpha$, deg^{-1}	k	C_p, J mol^{-1} K^{-1}	C_v, J mol^{-1} K^{-1}
trimethyl borate	1.656	1.084	1.502	1.528	137.2	89.8
triethyl borate	1.662	1.179	1.374	1.410	206.1	146.2
tripropyl borate	1.396	0.9950	1.126	1.403	215.4	153.5
triisopropyl borate	1.915	1.351	1.289	1.417	211.0	148.9
tributyl borate	1.251	0.8875	1.010	1.410	233.8	165.8
triisobutyl borate	1.403	0.9972	1.034	1.407	222.8	158.3

Table III. Experimental and Derived Data Involving the Calculation of A

	$10^3\eta$, P	$10^3\kappa$, J cm^{-1} s^{-1} K^{-1}	$10^{16}A$, s^2 mol^{-1}
trimethyl borate	3.544	1.885	1.146
triethyl borate	4.859	2.035	1.616
tripropyl borate	9.380	1.521	2.307
triisopropyl borate	7.502	1.412	2.873
tributyl borate	15.006	1.288	3.059
triisobutyl borate	16.430	1.139	3.942

established procedure with regard to the first member of most series of homologues, the trimethyl borate was omitted from this and all further correlations).

The molar refractions and parachors were deduced from eq 2 and 3, respectively. In view of the additive and constitutive nature of both R_D and P, the following correlations with R_a may be proposed:

$$R_a/R_D = 43.37 \pm 0.46 \quad (10)$$

$$R_a/P = 4.826 \pm 0.014 \quad (11)$$

$$R_D = 0.02470R_a - 3.797 \quad (12)$$

$$P = 0.2073R_a - 0.2897 \quad (13)$$

Equations 12 and 13 have a reproducibility of better than ±0.30%.

Molar heat capacities have not been reported in the literature for this class of compounds. Table II is a summary of all calculations involving heat capacities (k was derived from eq 4, and C_p from eq 7).

The heat capacities of the branched isomers are slightly lower than the corresponding straight-chain compounds, which is usually the case. From the data in Tables I and II, the following correlations may be deduced:

$$C_p = 0.02064R_a + 168.3 = 0.2191V_m + 166.4 \quad (14)$$

$$C_v = 0.01474R_a + 119.2 = 0.1555V_m + 118.1 \quad (15)$$

Equations 14 and 15 have a reproducibility of better than ±2.1%.

Table III lists all additional information needed for the calculation of the absorption coefficient, A, as defined by eq 8 (viscosities were taken from ref *2*, and thermal conductivities from data in ref *5*).

The effect of branching and the consequently larger molar volume is reflected in the slightly greater absorption shown by these isomers over the corresponding unbranched homologues. The following correlation between κ and C_p (in J g^{-1} K^{-1}) is indicated:

$$\kappa = (1.972 \times 10^{-3})C_p - 7.548 \times 10^{-4} \quad (16)$$

Equation 16 gives better than a ±2.0% reproducibility of the data.

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Registry No. Trimethyl borate, 121-43-7; triethyl borate, 150-46-9; tripropyl borate, 688-71-1; triisopropyl borate, 5419-55-6; tributyl borate, 688-74-4; triisobutyl borate, 13195-76-1.

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