Coefficient of Thermal Expansion of, and Sound Speed through, Nitromethane and Four Bis(difluoramino)alkanes

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Measurements have been made of the coefficients of thermal expansion of, and the sound speed through, the following liquids: nitromethane, 1,2-bis(difluoramino)propane, 2,2-bis(difluoramino)propane, 1,2-bis(difluoramino)butane, and 1,2-bis(difluoramino)-2-methylpropane. These results have been combined with previously measured or estimated heat capacities at constant pressure, C_p, for these liquids to obtain values for the heat capacities at constant volume, C_v. C_v for trinitrotoluene has been calculated from similar experimental values already reported.

THE HEAT CAPACITY at constant volume, C_v, is an important quantity in thermal explosion theory (*1, 4, 7*). It is difficult to measure C_v and it has been the practice to assume that C_v is equal to the heat capacity at constant pressure C_p.

The two heat capacities are related thermodynamically (*15*) by

$$C_p - C_v = -T\left(\frac{\partial v}{\partial T}\right)_p^2 \left(\frac{\partial v}{\partial p}\right)_T^{-1} \tag{1}$$

The thermodynamic equation for U, the velocity of sound through a substance (*12*), is

$$U^2 = -\left(\frac{v^2}{M}\right)\left(\frac{\partial p}{\partial v}\right)_S = -\frac{v^2}{M} \left[\left(\frac{\partial v}{\partial p}\right)_T^{-1} - \left(\frac{T}{C_v}\right)\left(\frac{\partial v}{\partial T}\right)_p^2 \left(\frac{\partial v}{\partial p}\right)_T^{-2}\right] \tag{2}$$

Eliminating $\left(\frac{\partial v}{\partial p}\right)_T$ from Equations 1 and 2 gives

$$C_v = \frac{C_p}{1 + [(MT\alpha^2U^2)(2.39 \times 10^{-8})/C_p]} \tag{3}$$

where M is the molecular weight, T is the temperature in ° K., α or $\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$ is the volumetric coefficient of thermal expansion in deg.$^{-1}$, U is the velocity of sound in cm. sec.$^{-1}$, and 2.39 × 10^{-8} converts the units from ergs to calories. C_v and C_p are in units of cal. mole^{-1} deg.$^{-1}$.

For solids (*21*) the difference between C_v and C_p is small. For example, in the case of copper at 20° C., $C_v = 5.7$ and $C_p = 5.9$ cal. mole^{-1} deg.$^{-1}$, a difference of about 3%. However, for liquids the approximation is not so good. From tables (*15*) of heat capacities at 25° C., for benzene $C_v = 23.0$ and $C_p = 32.5$ cal. mole^{-1} deg.$^{-1}$, for *n*-heptane $C_v = 41.8$ and $C_p = 53.0$ cal. mole^{-1} deg.$^{-1}$, for diethyl ether $C_v = 30.1$ and $C_p = 41.0$ cal. mole^{-1} deg.$^{-1}$, and for carbon tetrachloride $C_v = 21.8$ and $C_p = 31.6$ cal. mole^{-1} deg.$^{-1}$. In each case, C_v is about 70% of the corresponding C_p.

This article reports measurements at 25° C. of the coefficients of expansion and sound velocities of nitromethane (CH_3NO_2, NM); 1,2-bis(difluoramino)propane, [$CH_2(NF_2)CH(NF_2)CH_3$, 1,2-DP]; 2,2-bis(difluoramino)propane, [$CH_3C(NF_2)_2CH_3$, 2,2-DP]; 1,2-bis(difluoramino)butane [$CH_2(NF_2)CH(NF_2)CH_2CH_3$, 1,2-DB]; and 1,2-bis(difluoramino)-2-methylpropane [$(CH_3)_2CH(NF_2)CH_2NF_2$, IBA], a measurement of the heat capacity at constant pressure and 25° C. of 1,2-DP, and estimates of the C_p of the other bis(difluoramino)alkanes.

From the above results and previously reported data for nitromethane and trinitrotoluene, Equation 3 was used to calculate C_v for the six liquid explosives.

EXPERIMENTAL

Materials. Nitromethane was obtained from the Commercial Solvents Corp., San Jose, Calif. GLC analysis gave 96.5% nitromethane, 2.3% nitroethane, and 1.2% nitropropane. Karl Fischer analysis by E. Willis showed 0.1% water.

A solution of 1,2-DP in methylene chloride was obtained from Rohm and Haas. The methylene chloride was distilled off. The 1,2-DP was shown to be 99.0% pure by GLC.

A solution of 2,2-DP in the high-boiling chlorinated solvent, Arochlor 1248, was obtained from the Aerojet-General Corp. The 2,2-DP was distilled. No impurities could be detected by GLC, and it was inferred that the 2,2-DP was essentially 100% pure.

A solution of 1,2-DB in methylene chloride was obtained from the Naval Propellant Plant at Indian Head, Md. The methylene chloride was distilled and the residual 1,2-DB shown to be 99.0% pure by GLC.

A solution of IBA in Arochlor 1248 was obtained from Rohm and Haas. The IBA was distilled and shown to be 99.2% pure by GLC.

Heat Capacity at Constant Pressure. Eding has measured C_p of 1,2-DP at 25° C. to be 0.348 ± 0.005 cal. gram^{-1} deg.$^{-1}$, which corresponds to 51 ± 1 cal. mole^{-1} deg.$^{-1}$. This result has not been previously reported. The apparatus was a drop calorimeter (*2*). The values of C_p for the other bis(difluoramino)alkanes were estimated by comparison with their hydrocarbon analogs (*17*) to be 2,2-DP 51, 1,2-DB 58, and IBA 58 cal. mole^{-1} deg.$^{-1}$.

Coefficient of Expansion. Two 1-ml. (approximately) pycnometers were calibrated (*10*) at 20° C., using freshly distilled water. The calibration was checked using benzene (analytical reagent grade), and a value of 0.8816 gram ml.$^{-1}$ at 20° C. was obtained. This may be compared with values of 0.87893 gram ml.$^{-1}$ (*10*), 0.87890 gram ml.$^{-1}$ (*18*), and 0.87985 gram ml.$^{-1}$ (*20*). The experimental error of the density measurements is probably of the order of 0.002 gram ml.$^{-1}$.

Table I. Density as a Function of Temperature from NM, 1,2-DP, 2,2-DP, 1,2-DB, and IBA

Compound	Density, ρ, Grams Ml.$^{-1}$ 5° C.	15° C.	20° C.	25° C.	30° C.	35° C.	40° C.	$-10^3\left(\frac{\partial\rho}{\partial T}\right)$, Grams Ml.$^{-1}$ Deg.$^{-1}$	$10^3\alpha_{25} = \frac{-10^3}{\rho_{25}}\left(\frac{\partial\rho}{\partial T}\right)$, Deg.$^{-1}$	Ref.
NM	1.154	1.140		1.126		1.112		1.40 ± 0.00	1.24	This work
	1.156	1.141		1.128		1.114		1.39 ± 0.05	1.23	This work
			1.1382	1.1313	1.1244			1.377 ± 0.00	1.217	*(19)*
									1.321	*(8)*
1,2-DP	1.296	1.282		1.265			1.241	1.59 ± 0.07	1.26	This work
2,2-DP	1.288	1.270		1.254		1.236		1.72 ± 0.06	1.37	This work
	1.286	1.269		1.253		1.236		1.66 ± 0.03	1.32	This work
			1.259							*(14)*
1,2-DB	1.245	1.231		1.216		1.202		1.44 ± 0.03	1.18	This work
IBA	1.242	1.227		1.213			1.193	1.39 ± 0.05	1.15	This work

The densities of nitromethane (in duplicate), 2,2-DP (in duplicate), 1,2-DP, 1,2-DB, and IBA were measured at four temperatures between 5° and 40° C. (Table I). The slopes of the density-temperature plots were found by the method of least squares. The errors quoted in Table I are twice the standard deviations.

Velocity of Sound. The velocity of sound in nitromethane, 1,2-DP, 2,2-DP, IBA, and 1,2-DB was measured at 25° C. using the following technique *(6, 16)*. The liquid column varying in length from 4 to 12 mm. was contained in a Tygon vinyl tube 12.5 mm. in diameter. The tube was filled and air bubbles were removed by hypodermic needles. A PZT-4 piezoelectric transducer produced a sinusoidal 1-MHz. sec.$^{-1}$ mechanical wave at the bottom of the column. A similar transducer at the end of the column received the sound wave and reconverted it to electrical output. Oscilloscopic display showed directly the time for traverse of the liquid column. A precision time-sweep generator was used to allow measurement of the traverse time to ±0.01 μsec. The upper transducer was held in a sliding fixture which had a micrometer attached so that the column length could be measured to ±0.01 mm. The distance-time data were fitted by least squares to a straight-line velocity. A typical plot is in Figure 1. In the absence of liquid no signal was detected. The straight-line velocity did not go through the origin because of brass shims on the ends of the transducers and because of electronic delays.

The results, in units of mm. μsec.$^{-1}$, were 1,2-DP 0.96 ± 0.02, 2,2-DP 0.89 ± 0.03, IBA 0.90 ± 0.05, and 1,2-DB 1.00 ± 0.07. For nitromethane, the results of duplicate experiments run several weeks apart were 1.29 ± 0.05 and 1.31 ± 0.05 mm. μsec.$^{-1}$. These values are in good agreement with 1.34 *(3, 11)* and 1.28 mm. μsec.$^{-1}$ *(5)*.

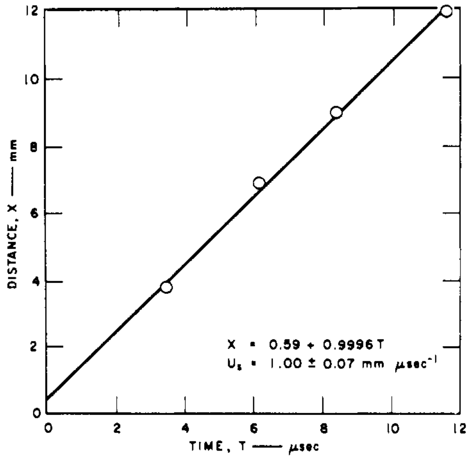

Figure 1. Measurement of velocity of sound in 1,2-DB

RESULTS AND DISCUSSION

The heat capacity at constant volume was calculated from Equation 3 for the six liquid explosives (Table II). The values of C_v are between 61 and 83% of the corresponding values of C_p.

Table II. Data for the Calculation of C_v

Compound	Mol. Weight	Temp., ° K.	$10^3\,\alpha$, Deg.$^{-1}$	Ref.	$10^{-5}\,U$, Cm. Sec.$^{-1}$	Ref.	C_p, Cal. Mole^{-1} Deg.$^{-1}$	Ref.	C_v, Cal. Mole^{-1} Deg.$^{-1}$
NM	61	298	1.22	[a]	1.30	[b]	25.4	*(9)*	17.8
TNT[c]	227	354	1.05	*(3)*	1.61	*(13)*	87	*(3)*	53.3
1,2-DP	146	298	1.26	[d]	0.96	[b]	51	[b]	39.3
2,2-DP	146	298	1.34	[d]	0.89	[b]	51	[e]	39.5
1,2-DB	160	298	1.18	[d]	1.00	[b]	58	[e]	45.5
IBA	160	298	1.15	[d]	0.90	[b]	58	[e]	47.9

[a] Table I, *(19)*.
[b] This work, see text.
[c] Trinitrotoluene, $CH_3C_6H_2(NO_2)_3$.
[d] Table I.
[e] Estimated, see text.

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Solubility of Lithium Bromide in Water between −50° and +100° C. (45 to 70% Lithium Bromide)

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The solubility curve between 45 and 70 weight % lithium bromide was studied and compared with published results. Solubility measurements were in good agreement with reported values obtained using the same technique. The addition of a small amount of lithium hydroxide or hydrogen bromide has a minimal effect on the solubility of lithium bromide.

THE SOLUBILITY of lithium bromide in water has been studied by many investigators as listed by Linke and Seidell (*6*), who point out that there is poor agreement among published values, especially in the range of interest to the air-conditioning field (*2*, *9*). The spread of these values is demonstrated in Figure 1, which illustrates why this system has remained a subject for continuing research.

The present study attempts to define the solubility curve, correlate the results with literature values, and show the effects of a small excess of lithium hydroxide and hydrogen bromide on the solubility, in the temperature range between −50° and +100° C. which encompasses a concentration of 45 and 75 weight % lithium bromide.

EXPERIMENTAL

Pure LiBr was prepared in solution from certified ACS HBr (Fisher Scientific Co.) and spectrographically pure Li_2CO_3 (Foote Mineral Co.). Recrystallized $LiOH \cdot H_2O$ or HBr was added to adjust the pH to 7. The pH of the neutral brine was measured on a diluted sample (1 part of brine to 10 parts of distilled water). The desired concentration was finally obtained by evaporation or addition of water to ensure the presence of both a solid and a liquid phase. The bromide ion concentration in the saturated solution was determined by titration techniques using standardized silver nitrate and potassium chromate as an indicator.

The solubility technique involved maintaining the solid and liquid phase together in a sealed polypropylene container submerged in a constant temperature bath for a minimum of 3 hours, with stirring. Samples maintained at constant temperature for a longer time (15 hours) did not give different values, indicating that equilibrium was attained. After the 3-hour period, the temperature of the mixture was measured at 1-hour intervals using copper-constantan thermocouples and a Wheatstone bridge.