High-pressure sound velocity and equation of state of aqueous solutions of hydroxylammonium nitrate and triethanolammonium nitrate

J. Frankel[a]; M. Doxbeck[a]

[a] Development and Engineering Center Close Combat Armaments Center Benet Weapons Laboratory, U.S. Army Armament Research, Watervliet, NY

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HIGH-PRESSURE SOUND VELOCITY AND EQUATION OF STATE OF AQUEOUS SOLUTIONS OF HYDROXYLAMMONIUM NITRATE AND TRIETHANOLAMMONIUM NITRATE

J. Frankel and M. Doxbeck
U.S. Army Armament Research, Development and Engineering Center
Close Combat Armaments Center
Benet Weapons Laboratory
Watervliet, NY 12189-4050

A cell for high pressure sound velocity measurements of liquids was designed and used in a Birch-Bridgman high pressure system with a liquid propellant specimen. The dependence of the sound velocity on pressure to 4.2 kbar (4200 atmospheres) was measured at room temperature and on temperature between 220 and 293 K at room pressure. These data, together with the temperature dependence of the specific heat which was also measured, and some thermodynamic arguments were used to obtain the full equation of state with temperature and the pressure dependence of the specific heat and of the volume expansivity at room temperature. We compare our results with data obtained by volumetric and other ultrasonic measurements.

INTRODUCTION

In the course of its utilization from storage to combustion, the propellant is subjected to intervals of high pressure up to an estimated 50,000 psi (3.4 kbars). We note that the thermodynamic

properties which control its use are not only temperature-dependent, but also density-dependent. It is therefore useful to know the equation of state (EOS) as a basis for further study of the pressure dependence of any thermodynamic properties of the material. Density-volume relations may be obtained directly by volume measurements as the pressure is changed isothermally,[1] or from the pressure dependence of the sound velocity[2] under isothermal conditions. The sound velocity at our frequencies ($\approx$ 10 MHz) gives adiabatic properties of the material whose thermodynamic state is defined by pressure and temperature. This forces us to distinguish between adiabatic and isothermal pressurizations of a system. In both cases we assume quasistatic, reversible processes, which are idealizations. For the adiabatic case, no heat enters or leaves the system and the temperature is allowed to increase, while for the isothermal case the temperature is constant, but heat is allowed to flow out of the system. The parameters to describe either system have to be adiabatic or isothermal respectively, and these quantities are not the same. The measurement of sound velocity in a system which is isothermally compressed gives us an adiabatic property (e.g. the compressibility from Eq. (1)) for a state which has been arrived at through isothermal processes. It is therefore necessary to convert the adiabatic property we obtain by measuring the velocity of sound in a state defined by P and T to an isothermal property referred to the same state. The equation which relates the sound

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velocity $v(T,P)$ to the adiabatic compressibility $K_S(T,P)$, which is defined as $-(1/V)(\partial V/\partial P)_S$ or $\frac{1}{\rho}(\frac{\partial \rho}{\partial P})_S$, and the density $\rho(T,P)$ is (in the absence of relaxation effects)

$$\frac{1}{K_S} = \rho v^2 \qquad (1)$$

The equation which takes us from an adiabatic to an isothermal description of the state is

$$K_T = K_S + \frac{TV\beta^2}{C_P} \qquad (2)$$

Here K_T is the isothermal compressibility, V is the volume per unit mass ($V = \frac{1}{\rho}$), C_P is the specific heat, T is the temperature in K, and β is the volume expansivity given by $(1/V)(\partial V/\partial T)_P$ or $-(1/\rho)(\partial \rho/\partial T)_P$. From Eqs. (1) and (2) we can get

$$(\frac{\partial V}{\partial P})_T = - \frac{TV^2\beta^2}{C_P} - \frac{V^2}{v^2} \qquad (3)$$

If Eq. (3) is integrated, a relationship between the change of density and pressure[3] can be obtained at constant temperature T.

$$\rho(P) - \rho(P_0) = \int_{P_0}^{P} \frac{dP}{v^2} + \int_{P_0}^{P} \frac{T\beta^2}{C_P} dP \qquad (4)$$

The pressure dependence of the sound velocity which is necessary for evaluation of the first integral on the right-hand side is available from our measurement. The pressure dependence of β and C_P can be obtained from thermodynamic considerations:

$$(\frac{\partial \beta}{\partial P})_T = - (\frac{\partial K_T}{\partial T})_P \qquad (5)$$

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where

$$K_T(T) = \frac{1}{\rho(T)} \left[\frac{1}{v^2(T)} + \frac{T\beta^2(T)}{C_p(T)} \right] \qquad (6)$$

The temperature dependence for each quantity on the right-hand side of Eq. (6) is available for LP 1845. We have $\rho(T)$ or $\beta(T)$ from Messina et al.[4] for LP 1845 and $C_p(T)$ and $v(T)$ from our own measurements for our nominal 1845 mixture (see Table 1). If we use Messina's data as appropriate for our mixture

$$\rho(T) - \rho(0°C) = -0.0007119 \ T \qquad (7)$$
and
$$v(T) = 1966 - 1.703 \ T \qquad (8)$$

where ρ is in gm/cm³, T is in °C between -60 and +23, and v is in m/sec. The value of C_p at room temperature is 2.29 joules/gm°C. Hence, $(\frac{\partial K_T}{\partial T})_p$ for Eq. (5) yields 5.2×10^{-8}/°C bar. Therefore, the pressure dependence of the volume expansivity for room temperature is given by

$$\beta = 4.898 \times 10^{-4} - 5.20 \times 10^{-8} \ P \qquad (9)$$

in units of K^{-1}. The pressure dependence of the specific heat C_p can be found from[5]

$$(\frac{\partial C_p}{\partial P})_T = - \ T \ (\frac{\partial^2 V}{\partial T^2})_p \qquad (10)$$

We have $\rho(T)$ from Eq. (7), V is the specific volume ($= 1/\rho$), and

$$(\frac{\partial^2 V}{\partial T^2})_p = - \frac{1}{\rho^2} \ (\frac{\partial^2 \rho}{\partial T^2})_p + \frac{2}{\rho^3} \ (\frac{\partial \rho}{\partial T})_p^2 \qquad (11)$$

Therefore, from Eqs. (7), (10), and (11)

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$$\left(\frac{\partial C_p}{\partial P}\right)_T = -\frac{2T}{\rho^3}\left(\frac{\partial \rho}{\partial T}\right)_P^2 = -9.78 \times 10^{-6} \text{ joules/gm}^\circ\text{C-bar} \qquad (12)$$

$\partial K_T/\partial T)_P$ in Eq. (5) equals the pressure derivative of the expansivity only in the vicinity of P, the pressure at which $(\partial K_T/\partial T)_P$ is evaluated. In our case, the pressure is P_0, atmospheric pressure. More generally, for higher P, the pressure dependence of the expansivity should be written as

$$\beta(P) = \beta(P_0) + P\left(\frac{\partial \beta}{\partial P}\right)_{P_0} + \frac{P^2}{2!}\left(\frac{\partial^2 \beta}{\partial P^2}\right)_{P_0} + \dots \qquad (13)$$

Here we only use the first two terms of Eq. (13). We assume no great curvature in β, so that $\partial^2\beta/\partial P^2)_{P_0} \ll \partial\beta/\partial P)_{P_0}$. An equation similar to Eq. (13) for $C_p(P)$ would also be correct, and similar arguments would apply, and $\frac{P^2}{2!}\left(\frac{\partial^2 C}{\partial P^2}\right)_{P_0}$ is thought to be much smaller than the retained terms.

EXPERIMENTAL DETAILS

A mixture of hydroxylammonium nitrate (HAN), triethanolam-monium nitrate (TEAN), and water was prepared whose composition is given in Table 1. Compositions of 1845 and 1846 mixtures are given for comparison.

TABLE 1. Liquid Propellant Compositions

	Wt. % HAN	Wt. % TEAN	Wt. % H_2O
1845	63.2	19.9	16.8
present	62.3	19.6	18.1
1846	60.8	19.2	20.0

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The Birch-Bridgman system was built by the Harwood Corporation.* A high pressure oil was used to transmit pressure to the specimen. The pressure was measured to better than 1.5 percent by means of a manganin coil built in the bottom closure of the high pressure cell. This coil was calibrated by means of another coil which had been calibrated with a dead weight tester.

A cell was designed and built to measure liquid sound velocities in a high pressure environment (Figure 1). This cell was also used to measure the temperature dependence of the sound velocity. It has a threaded right circular cylinder (the buffer) 0.5 inch in diameter which separates the transducer from the specimen. Faces A and B of the buffer are plane parallel. A 10 MHz lithium niobate transducer is bonded to face A, and face B is in contact with the liquid specimen. Face C of the reflector is parallel to the other two faces and remains at a fixed known distance from face B. For this purpose the buffer is threaded into the threaded holding ring and the spacer and reflector are pushed up against it by a threaded disk which has a ball-like protrusion in the center. This and the reflector have small openings near their edges which allow the specimen liquid to travel from below the threaded disk to the specimen chamber. The separator membrane seen in Figure 1 serves as a separator and pressure transmitter between the specimen and the pressurizing oil in the Birch-Bridgman cell. The

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*Harwood Corporation, Walpole, MA.

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ultrasonic transducer is pulsed with a broadband gated amplifier. Ultrasonic pulses are produced in the buffer, travelling at right angles to faces A and B. As a pulse impinges on B, a part is reflected back to A and the remaining part travels through the liquid specimen and is reflected back and forth between B and C. After each traverse, again at face B, part of the pulse is transmitted and proceeds to face A and is sensed by the trans- ducer. From there it is amplified by a broadband receiver. The amplified signal is displayed on a Tektronix 7704A oscilloscope where the time delay measurements are made to a resolution of about 5 nsec. The sound velocity thus obtained in our mixture to 4.2 kbar at room temperature is shown in Figure 2.

DATA ANALYSIS AND ROOM TEMPERATURE EQUATION OF STATE

We use Eq. (4) to determine density where β and C_P are linear with pressure. The sound velocity in m/sec was fit to pressure (in bars) using a singular value decomposition least square fit program[6,7] and can be given by

$$v = 1942.79 + 0.154\ P - 6.482 \times 10^{-6}\ P^2 - 1.638 \times 10^{-10}\ P^3 \quad (14)$$

We measure the velocity with a variance of $\sim$ 2 m/sec. The standard error of estimate of our measurements from Eq. (14) is 4.66 m/sec. In order to evaluate the integrals in Eq. (4) we used Bode's rule.

$$\int_{x_0}^{x_4} f(x)\ dx = \frac{2h}{45}\ [7f_0 + 32f_1 + 12f_2 + 32f_3 + 7f_4] \quad (15)$$

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For the second integral in Eq. (4), we used the linear pressure dependence of the specific heat. The specific heat at 1 atm. is correct to ± one percent. This leads to a variance of ~ 10^{-2} J/gm°C, in C_p which leads to a variance in the density of ~ 10^{-4} gm/cm³. Using Eqs. (4), (7), (9), (12), (14), and (15), the room temperature equation of state (Figure 3) was calculated to be:

$$\rho = 1.453 + 2.938 \times 10^{-5}\ P - 2.171 \times 10^{-9}\ P^2 + 1.219 \times 10^{-13}\ P^3 \qquad (16)$$

Figure 4 shows the fit of the EOS data by means of the Tait Equation, $B = -V_0\ \dfrac{dP}{dV}$. For the Tait Equation, the fit gives:

$$B = 48.68 + 10.85\ P \qquad (17)$$

where B (the bulk modulus) and P are in kbar.

DISCUSSION

In Figure 2 we present the results of the sound velocity dependence on pressure. For comparison we also have Costantino's data for LP 1845, also taken at room temperature, but obtained with volumetric measurements. The comparison indicates a difference which increases systematically with pressure, the values starting initially alike, and then increasing to a difference of about 25 m/sec (one percent) at 4 kbar. From the variance given for both measurements, this difference is acceptable. It is interesting, however, to speculate on other possible reasons. The small difference in composition of our mixture from LP 1845 can not explain the difference since Costantino also measured LP 1846

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and our velocity measurements are lower than both of his LP 1845 and 1846 values, even though our composition is between them. The possibility also exists of heating due to adiabatic compression of the specimen (due to heating wihout any dissipation of heat from the specimen). We consider the specimen mass only. The temper- ature increase associated with an adiabatic compression only, is given by $\Delta T = \frac{TV\beta}{C_P} \Delta P$. In our case at room temperature T = 296 K, with V = 0.668 cm³/gm, C_P = 229 Ncm/gmK, $\beta = 4.9 \times 10^{-4} K^{-1}$, for an adiabatic increase in pressure due to 4000 atmospheres (4.05 N/cm²), the temperature increase is +16 K, i.e., from 23 to 39 C. From our own Eq. (8), we have the temperature coefficient of the velocity at room pressure. If we assume the same temperature coefficient at all pressures, then the drop in velocity due to this temperature increase is about 1.1 percent. This change is of the correct magnitude to explain the difference, but an attempt was made in our measurement to allow the temperature to stabilize. Data as presented was taken on the up, as well as the down pressure cycle in several runs and no discernible difference was found in the values at high pressure, as well as at zero pressure, before and after the pressure cycling. Each full up and down pressure cycle took about 50 minutes. The equation of state com- parison (Figure 3) also shows a difference (which cannot be accounted for by the velocity difference). At 4 kbar our change of density from zero pressure is about 6.2 percent, whereas Costantino's is about 5.0 percent.

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This small difference is not surprising, considering that it was arrived at through different physical measurements and calculations, but it would be gratifying to know the reason. We wanted to check the possibility that the increased viscosity of the liquid could alter Eq. (1), but we were unsuccessful in getting a shear wave through the liquid at pressure, therefore we tentatively conclude that relaxation phenomena are not reflected in the density difference.

TABLE 2. Pressure and Temperature Dependence of Thermodynamic Quantities* (Obtained Here)

Equation	Units
$v(T) = 1966 - 1.703T$	m/sec,°C
$K_T(T) = 1.954 \times 10^{-5} + 5.200 \times 10^{-8}T$	bar^{-1},°C
$v(P) = 1942.79 + 0.154P - 6.482 \times 10^{-6}P^2 - 1.638 \times 10^{-10}P^3$	m/sec,bar
$\rho(P) = 1.4532 + 2.9387 \times 10^{-5}P - 2.1711 \times 10^{-9}P^2 + 1.2192 \times 10^{-13}P^3$	gm/cm^3,bar
$B(P) = 48679 + 10.848P$ (Tait Equation)	bar,bar
$C_P(P) = 2.29 + 9.78 \times 10^{-6}P$	joules/ gm K,bar
$\beta(P) = 4.898 \times 10^{-4} - 5.20 \times 10^{-8}P$	K^{-1},bar
$K_T(P) = 2.02 \times 10^{-5} - 3.38 \times 10^{-9}P + 3.36 \times 10^{-13}P^2$	bar^{-1},bar

*Pressure dependence found at room temperature (23°C). Temperature dependence found at one atmosphere.

THE FULL PVT THERMODYNAMIC DESCRIPTION OF THE FLUID

So far we have obtained the thermodynamic quantities given in Table 2. These expressions only hold for the phase regions where the propellant remains a homogeneous mixture of its constituents, where we have no phase changes and no phase separation, and, less stringently, no change in viscosity.

A homogenous isotropic system under hydrostatic pressure obeys the following

$$\frac{dV}{V} = \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T dP + \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P dT \tag{18}$$

This becomes

$$\int_{V_0}^{V} \frac{dV}{V} = - \int_{P_0}^{P} K_T(P) dP + \int_{T_0}^{T} \beta dT \tag{19}$$

If we know the initial state P_0, V_0, T_0, we can then obtain the equation of state relation at any other PVT. In our case, it is convenient to follow the procedure of evaluating the first integral on the RHS from $\rho(P)$ or $K_T(P)$ (both given in Table 2) from room pressure P_0 to the desired pressure P, and then use the pressure dependent β obtained from Table 2, also in the second integral on the RHS. This integral is evaluated from room temperature to the desired temperature T. A fit to the results of our calculation and data gives us the following relationship for the PVT equation of our fluids under the constraints discussed in this paper.

$$\frac{V}{V_0} = \exp[-\{+2.02 \times 10^{-8} P - 1.69 \times 10^{-9} P^2 + 1.12 \times 10^{-13} P^3 - 1.90 \times 10^{-18} P^4\}$$
$$+ 4.898 \times 10^{-4}(T-T_0) - 5.2 \times 10^{-8} P(T-T_0)] \tag{20}$$

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Figure 5 also shows several PV curves at different tem-
peratures. We now have a full thermodynamic description of our
propellant, which is based on the approximations and techniques
discussed here. Further equation of state determinations and
viscosity measurements with temperature and pressure will be
carried out to increase the reliability of these predictions.

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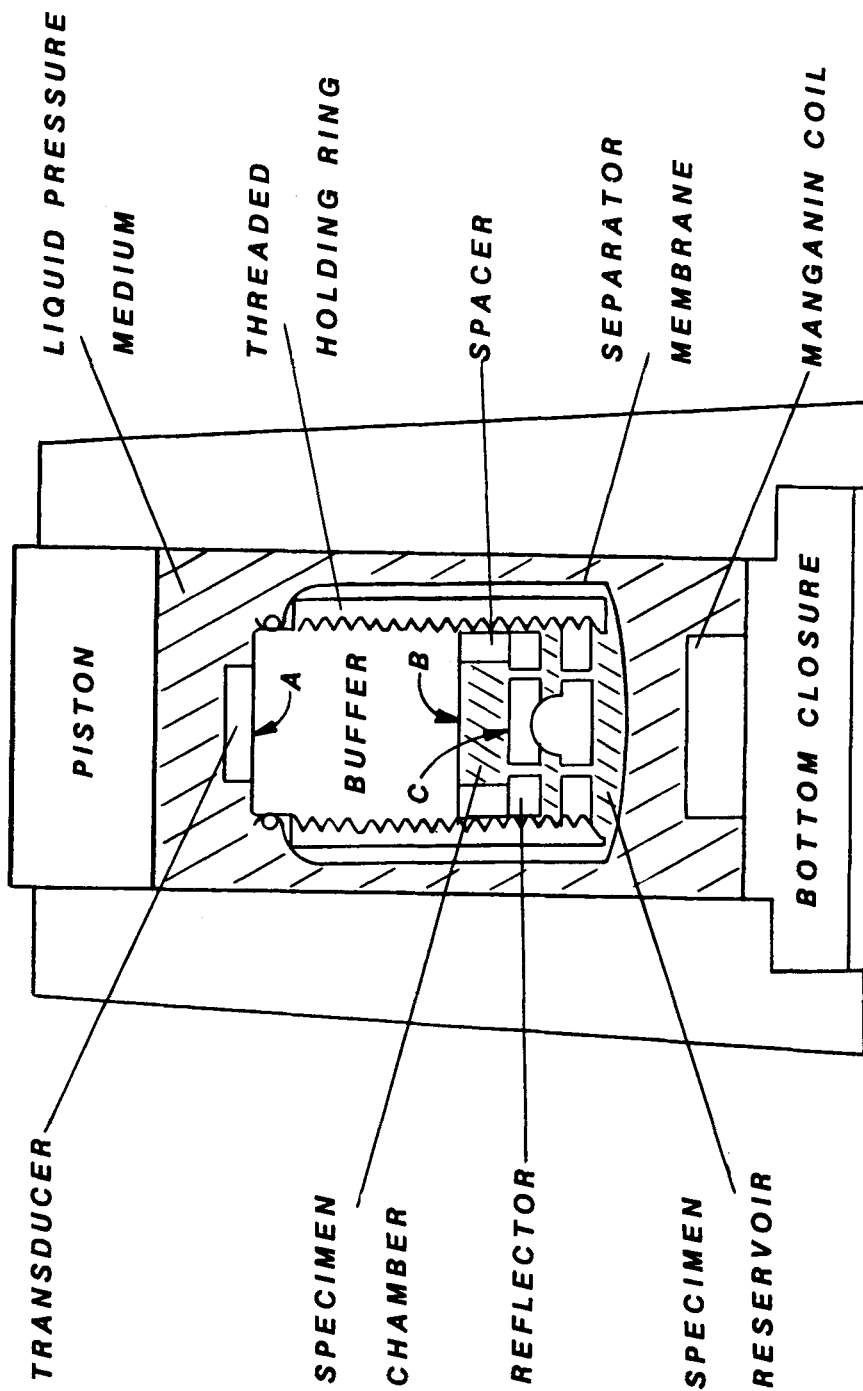   Mathematical Computations," Prentice-Hall, Englewood Cliffs,
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LIQUID PRESSURE

MEDIUM

THREADED

HOLDING RING

SPACER

SEPARATOR

MEMBRANE

MANGANIN COIL

PISTON

A

BUFFER

B

C

BOTTOM CLOSURE

TRANSDUCER

SPECIMEN

CHAMBER

REFLECTOR

SPECIMEN

RESERVOIR

FIGURE 1

Schematic of the ultrasonic cell.

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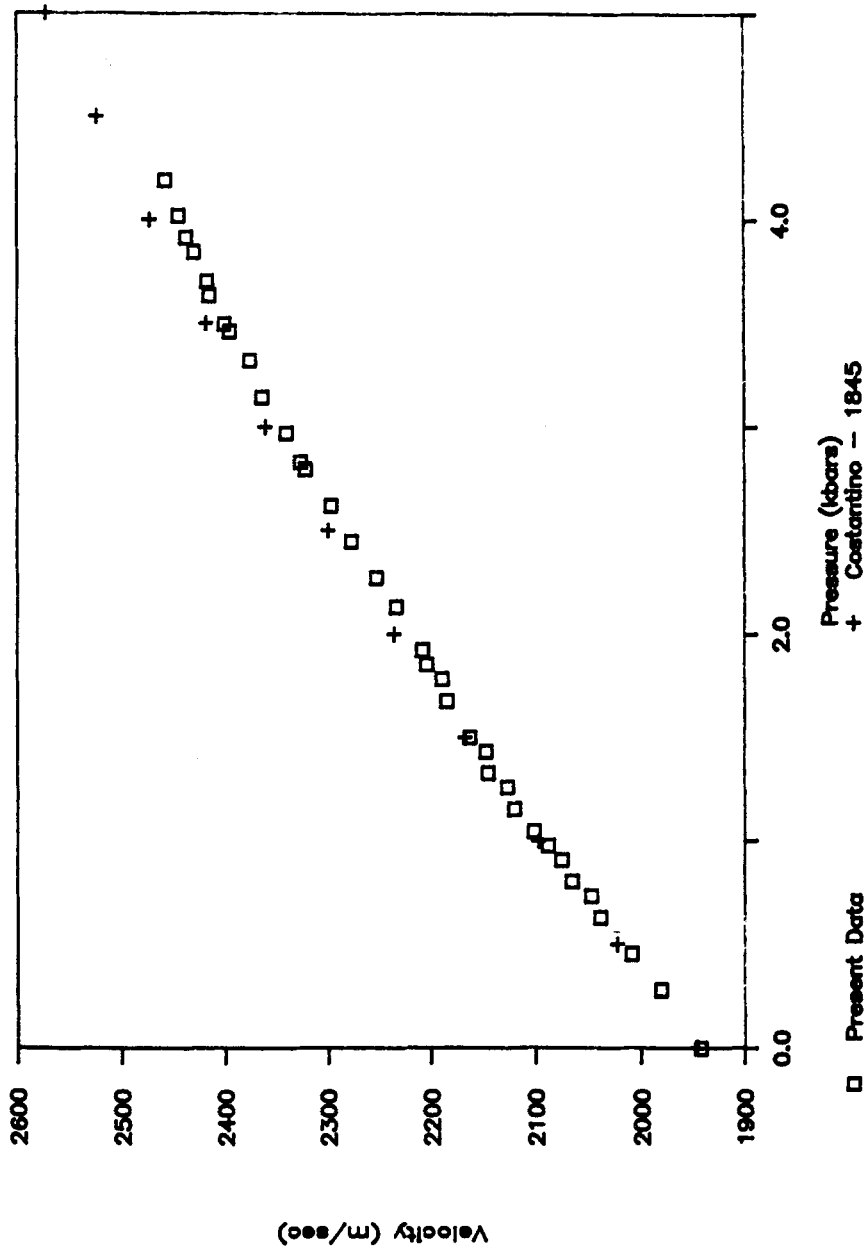
Comparison of Velocity Data

FIGURE 2

Comparison of the pressure dependence of the longitudinal sound
velocity with costantino's data.

Pressure (Kbars)
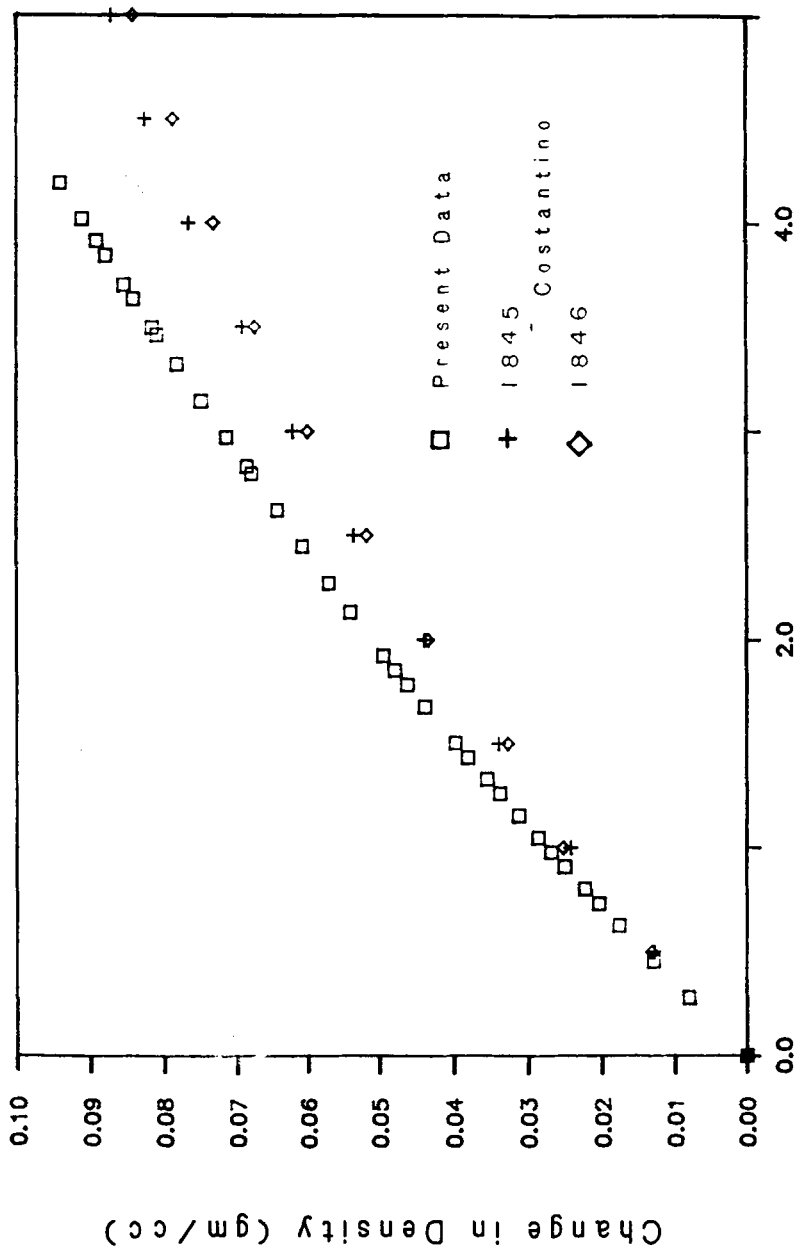
FIGURE 3

Comparison of the change of density results from our analysis
based on sound velocity data, and Costantino's volumetric
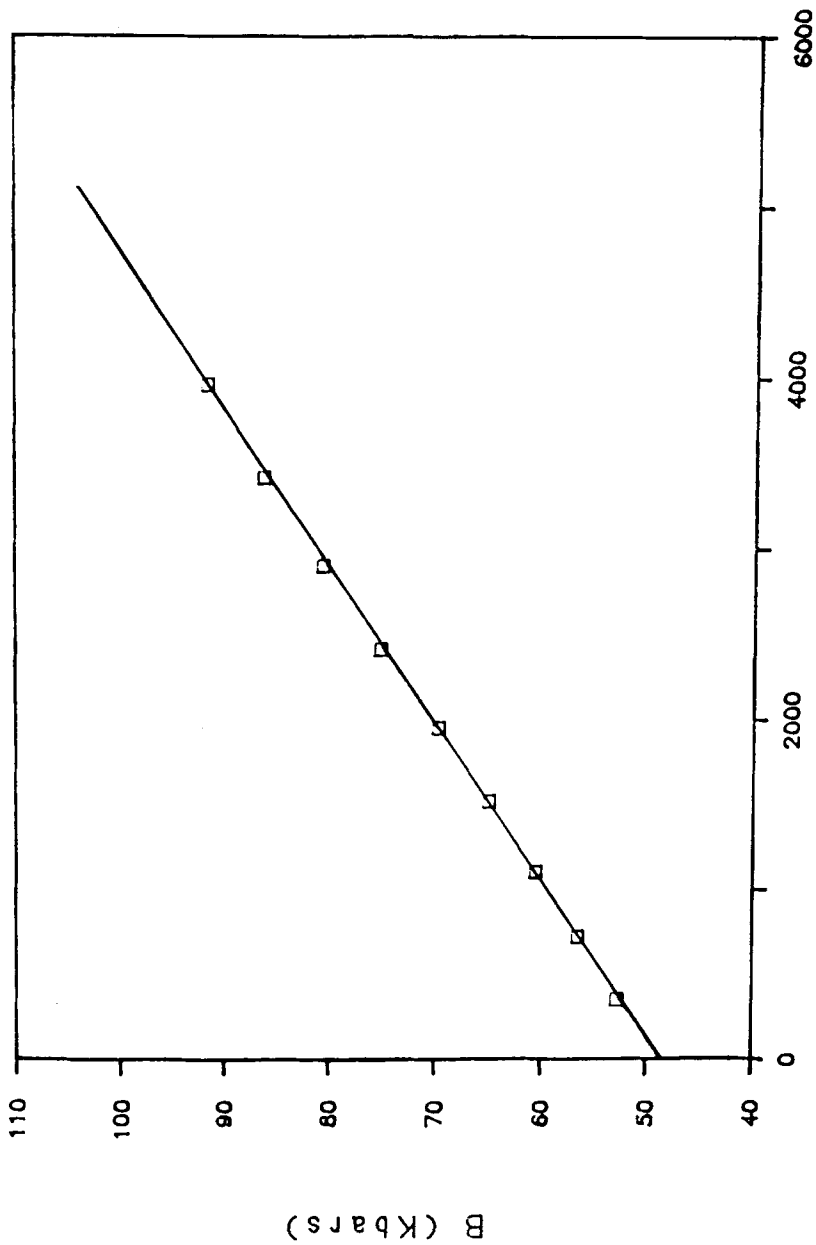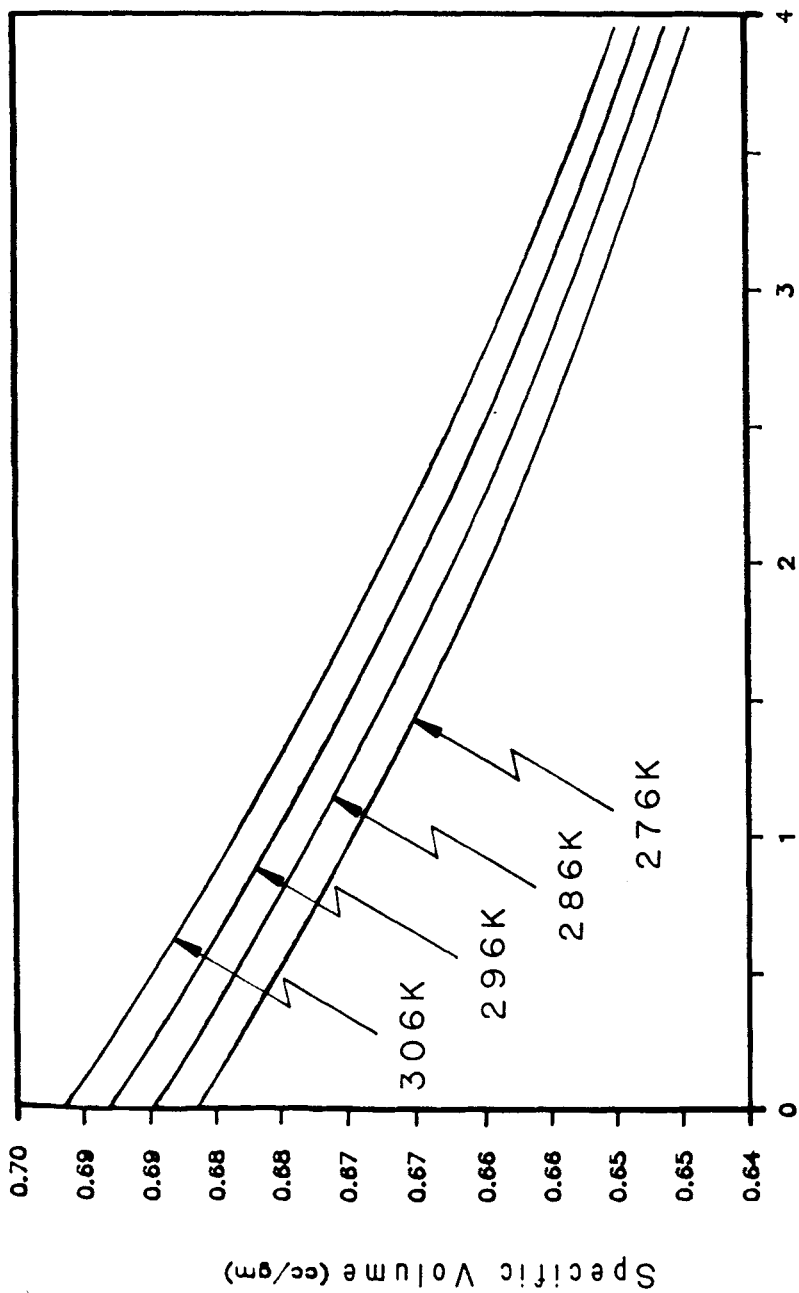measurements.

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Tait Equation

Pressure (bar)

B (Kbars)

Correlation Coeff. $R^2 = 0.984$

The linear relationship between the bulk modulus $B = V_n(\partial P/\partial V)_T$

FIGURE 4

Pressure (Kbars)

FIGURE 5

Curves giving the pressure dependence of the volume at different temperatures, resulting from our analysis.

Specific Volume (cc/gm)

306K
296K
286K
276K

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