ON AN ACOUSTIC METHOD FOR THE DETERMINATION OF THE DENSITY OF A LIQUID AS A FUNCTION OF PRESSURE

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On the basis of Schaaffs paper and Grüneisen's theory it has been shown that the Rao expression at constant temperature does not depend on the pressure. It results from the stability of the Rao-Schaaffs expression that it is possible to determine the density of a liquid as a function of pressure by the intermediary of quantities measured exclusively under normal pressure. The method provides a better agreement of the calculated values with experimental ones than do other methods.

1. Introduction

A precise determination of the density of a liquid as a function of the temperature T and the pressure p can be reduced to the hitherto unsolved problem of the liquid state equation. Although there exist many empirical or semi-empirical liquid state equations, none of these permits determination of the volume (or the density) with satisfactory accuracy over broad intervals of pressures and temperatures. In addition, these equations are predominantly specific rather than universal.

The generally valid thermodynamical differential equations do not help in solving the problem since the values of the partial derivatives of the parameters of the liquid state are unknown. Thus resort must be made, with the present state of knowlegde, to the semi-empirical equations. The choice of an equation is purely arbitrary and depends, for example, on the kind of liquid and the relevant interval of temperatures and pressures. The determination of the relationship $V = V(p, T)$ in extreme conditions now assumes a special importance with a view to the operating conditions of engine fuels and lubricants in aviation and rocket technology.

It should be noted that WEHR [1] and SZACHNOWSKI [2] have, for a long time been engaged in the problem of the determination of the density of a liquid as a function of the pressure. For various aviation fuels and oils they have

succeeded in achieving satisfactory agreement with experimental results by assuming that the ratio of the specific heats in pressure intervals of the order of several hundred atmospheres is constant. Such an assumption is not valid for greater pressure changes and thus the continuation of the work started by WEHR is not possible. The theoretical solution of the problem of the dependence of $\varkappa$ on the pressure is not possible with the knowledge available([1]), while the experimental material regarding this problem is very poor.

In this situation it has been decided to resume work on the determination of the density of a liquid as a function of pressure, but with an acoustic method, because of the high efficiency and accuracy of present-day ultrasonic measurement techniques. The starting point is the empirical fact stated recently by SCHAAFFS that the so-called Rao expression — which has so far been investigated at constant atmospheric pressure as a function of temperature — has proved to be independent of the pressure for a constant temperature.

2. The independence of Rao's formulation from the pressure

Using the results of measurements of sound velocity and density made by RAJAGOPALAN, CARNEVAL and LITOVITZ for n-heptane, n-octane, n-nonane, n-decane and n-dodecane, and for methyl, ethyl, propyl and n-butyl alcohols, as well as the results obtained by VEDAM and HOLTON for water, SCHAAFFS has stated that the so-called Rao expression is essentially independent of pressure, especially for pressures above 1000 atm.

Some results of his calculations are given in Table 1. The measurements were made at a temperature of 20°C.

Table 1

Substance	p [atm]	$R_p \times 10^{-3}$ [cm$^{10/3}$s$^{-1/3}$mol^{-1}]	Substance	p [atm]	$P_p \times 10^{-3}$ [cm$^{10/3}$s$^{-1/3}$mol^{-1}]
n-heptane	1	7.13	n-dodecane	1	11.50
	785	7.32		785	11.80
	1370	7.36		1370	11.90
Methyl alcohol	1	1.943	ethyl	1	2.85
	1000	2.012	alcohol	1000	2.95
	2000	2.022		2000	2.96
n-propyl alcohol	1	3.670	n-octane	1	8.00
	3000	3.870			
	8000	3.915		785	8.21
	10000	3.925		1370	8.28

([1]) Thermodynamics provides no temperature and pressure dependence of the specific heat and no such relation should be expected to be stated since the material constants are a consideration of importance. The situation is identical to that for the problem of the liquid state equation. Thermodynamics is not capable of providing such an equation (C. SCHÄFER, *Introduction to theoretical physics*, vol. II).

SCHAAFFS [3] was investigating the expression

$$R_p = w^{1/3}\left(\frac{M}{\varrho}\right),$$

where w is the sound velocity, ϱ is the liquid density and M is the molar mass.

However, it is known that in the range of variable temperatures and constant pressures more exact results are obtained by using, for the determination of various molecular quantities, the individual power exponent according to KUCZERA [4, 5, 6]. An attempt has therefore been made to investigate the dependence of the Rao expression by using the individual value of the power exponent determined for normal pressure.

In the calculations use has been made of the results of measurements of the sound velocity and the density for n-pentane over a pressure range from 1 to 8000 atm, contained in the papers by IKRAMOW and BIELIŃSKI [7].

The results of these calculations are presented in Table 2.

Table 2

Δp [atm]	$R_p \times 10^{+4}$	Remarks
0	13.4	
500	13.8	1. Measurements were made at a temperature of 20°C
1000	13.8	
1500	13.7	2. The maximum error R_p is ± 1.5 %
2000	13.8	
2500	13.8	3. In the calculations the individual power exponent has
3000	13.8	been used
3500	13.8	$q = 2.83$
4000	13.9	
4500	13.8	$q = \dfrac{\dfrac{1}{w}\left(\dfrac{\partial w}{\partial T}\right)_{p_1}}{\dfrac{1}{v}\left(\dfrac{\partial v}{\partial T}\right)_{p_1}}$
5000	13.9	
5500	13.8	
6000	13.8	
6500	13.8	$p_1 =$ normal pressure
7000	13.8	
8000	13.9	

It can be seen that the application of an individual exponent gives a better stability of the expression $R_p = w^{1/q}(M/\varrho)$ with changing pressure and constant temperature.

Accidental deviations are the result of errors made during the measurement. Worthy of note, although so far unexplained, is the fact that for all high pressures the exponent q has remained unchanged.

3. An attempt to explain the independence of the Rao expression from the pressure

Let us consider, following GRÜNEISEN [8] and others, the liquid molecules as point sources of force arranged momentarily along a certain direction at distances $\bar{r}$ and bonded by intermolecular forces. When a molecule is shifted by ξ, then the force of the interaction of two nearest molecules is $f \approx 2\xi f'(\bar{r})$. Let us assume that neighbouring molecules are distributed evenly on spheres of radii $S_i \bar{r}$. The force of interaction from the neighbours distributed along a certain considered direction is $2\xi \sum_i (S_i \bar{r})$. If we denote $\frac{1}{2}\cos^2 \varphi_i = t_i$, where φ_i are the angles to the chosen direction, then the force of interaction from all the neighbours will be $f = 2\xi \sum_i t_i f'(S_i \bar{r})$.

The potential of the interaction is expressed by equation

$$\varphi(r) = -\frac{\alpha}{r^x} + \frac{\beta}{r^y}, \tag{1}$$

where x and y are constants $(y > x)$, and α and β are individual constants.

In considering equation (1), the directing force D is

$$D = \frac{f}{\xi} = 2\left\{ y(y+1)\frac{\beta}{\bar{r}^{y+2}} \sum_i \frac{t_i}{S_i^{y+2}} - x(x+1)\frac{\alpha}{\bar{r}^{x+2}} \sum_i \frac{t_i}{S_i^{x+2}} \right\}. \tag{2}$$

We write

$$\left(\sum_i \frac{p_i}{S_i^x} \right)\alpha = a \quad \text{and} \quad \left(\sum_i \frac{p_i}{S_i^y} \right)\beta = b,$$

where p_i is the number of neighbours as a distance $S_i \bar{r}$.

It should be noted that in the equilibrium state

$$\frac{ax}{\bar{r}_0^{x+1}} = \frac{by}{\bar{r}_0^{y+1}}.$$

Then

$$D = 2\frac{ax}{\bar{r}^{x+2}} \left\{ \left(\frac{\bar{r}_0}{\bar{r}} \right)^{y-x} (y+1)\,\Psi(y) - (x+1)\,\Psi(x) \right\}, \tag{3}$$

where

$$\Psi(y) = \frac{\displaystyle\sum_i \frac{t_i}{S_i^{y+2}}}{\displaystyle\sum_i \frac{p_i}{S_i^y}} \quad \text{and} \quad \Psi(x) = \frac{\displaystyle\sum_i \frac{t_i}{S_i^{x+2}}}{\displaystyle\sum_i \frac{p_i}{S_i^x}}.$$

Let us derive the GRÜNEISEN factor $\gamma = d\ln\nu/d\ln v$, which as GRÜNEISEN has proved experimentally, does not depend on the temperature and pressure.

Since the frequency of vibration of the molecules ν, assuming a monochromatic vibration spectrum, is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{D}{\mu}},$$

we have

$$d(\ln \nu) = \frac{1}{2} d(\ln D) \quad \text{and} \, \nu = \text{const}\, \bar{r}^3,$$

where D is the directing force, and μ the oscillator mass, so $d(\ln \nu) = 3\, d(\ln \bar{r})$. Consequently,

$$\gamma = -\frac{d(\ln \nu)}{d(\ln v)} = -\frac{1}{6} \frac{d(\ln D)}{d(\ln \bar{r})}. \tag{4}$$

If we assume $\bar{r}_0 \approx \bar{r}$ (the increase of temperature will indeed cause an increment in $\bar{r}$, but the increase in pressure will reduce this increment in $\bar{r}$), it can be shown that

$$\gamma = \frac{1}{6} \frac{(y+2)(y+1)\Psi(y)-(x+2)(x+1)\Psi(x)}{(y+1)\Psi(y)-(x+1)\Psi(x)}. \tag{5}$$

If we take into consideration the interaction of all the more distant neighbours, then $\Psi(x) \approx 0$ and $\Psi(y) \approx 1/9$. Consequently,

$$\gamma = \frac{1}{6}(y+2). \tag{6}$$

According to BORN-KÁRMÁN the velocity of wave propagation is expressed by the formula

$$w = r \sqrt{\frac{D}{\mu}} = 2\pi r \nu_m \cdot (^2) \tag{7}$$

Since

$$r = \sqrt[3]{\frac{v}{kN_A}},$$

where v denotes the molar volume, k is the structural factor, which is independent of pressure and temperature, and N_A is the Avogadro number, hence after logarithmic differentiation we obtain

$$d(\ln w) = \tfrac{1}{3} d(\ln v) + d(\ln \nu_m),$$

i.e.

$$\frac{d(\ln w)}{d(\ln v)} = \frac{1}{3} + \frac{d(\ln \nu_m)}{d(\ln v)}. \tag{8}$$

(²) According to Eucken, for normal monochromatic body the limiting frequency of the spectrum is $\nu_m \approx \nu$.

Substituting equation (6) into equation (8), we obtain

$$\frac{d(\ln w)}{d(\ln v)} = \frac{1}{3} - \frac{1}{6}(y+2) = -\frac{y}{6}$$

or

$$\frac{\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_T}{\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T} = -\frac{y}{6} = -q. \tag{9}$$

In integral form, expression (9) becomes

$$w^{1/q}\left(\frac{M}{\varrho}\right) = R_p = \text{const.} \tag{10}$$

In this manner we obtain the analogue of Rao's expression which is valid for $T = \text{const}$, as distinct from the classical rule which can be applied for $p_i = \text{const}$ with a universal power exponent $q = 3$. Expression (10) is certainly an approximate form of more complex, but as yet unknown relations between the sound velocity and the liquid volume.

4. Consequences of the Rao-Schaaffs rule

It will be demonstrated that, from the stability of the Rao-Schaaffs expression, it is possible to determine the liquid density as a function of pressure using quantities measured exclusively under normal conditions.

For this purpose we may observe that

$$w^2 = \left(\frac{\partial p}{\partial \varrho}\right)_s, \tag{11}$$

hence

$$p_1 - p_2 = \int_{\varrho_1}^{\varrho_p} w^2 \partial \varrho,$$

where ϱ_1 denotes the density at pressure p_1, and ϱ_p is the density at pressure p.

Since

$$R_p = w_1^{1/q}\left(\frac{M}{\varrho_1}\right) = w^{1/q}\left(\frac{M}{\varrho}\right), \tag{10'}$$

the substitution of equation (10') into equation (11) and subsequent integration imply

$$p - p_1 = \frac{w_1^2 \varrho_1}{2q+1}\left[\left(\frac{\varrho_p}{\varrho_1}\right)^{2q+1} - 1\right]. \tag{12}$$

From (12) it is possible to determine the density ϱ_p as

$$\varrho_p = \varrho_1 \sqrt[2q+1]{(2q+1)\frac{p-p_1}{w_1^2 \varrho_1} + 1}. \tag{13}$$

It can be seen that in formula (13) there are only the quantities measured at normal pressure.

When we assume $q = 3$ ([3]) a universal power exponent in expression (10'), equation (13) takes the form

$$\varrho_p = \varrho_1 \sqrt[7]{\frac{7(p - p_1)}{w_1^2 \varrho_1} + 1}. \tag{13a}$$

If we neglect the pressure p_1, as being considerably smaller than p, then equation (12) can be written in the form

$$p = \frac{1}{7} w_1^2 \varrho_1 \left[\left(\frac{\varrho_p}{\varrho_1} \right)^7 - 1 \right]. \tag{12a}$$

KIRKWOOD [9] obtained an analogous equation empirically in the form

$$p = B(S) \left[\left(\frac{\varrho_p}{\varrho_1} \right)^n - 1 \right], \tag{14}$$

where $B(S)$ and n are constants for a given liquid.

Equation (14) applies well for water within the range of pressures from 1 to 25000 atm for $n = 7.15$.

Taking advantage of relation (13), the density has been calculated for n-heptane and for diethyl ether over a broad range of pressures and at ambient temperature. The results have been compared with experimental data. Results of these calculations are shown in Tables 3 and 4.

Table 3. The calculation of the density of n-pentane at a temperature of 20°C

p [atm]	ϱtable [g/cm³]	ϱcalculated Eq. (13a)	Devia-tion [%]	ϱcalculated Eq. (13)	Devia-tion [%]	Remarks
1	0.6254	—	—	—	—	1.In formula (13a) the
500	0.6660	0.664	−0.30	0.665	−0.15	exponent $q = 3$
1000	0.7044	0.693	−1.62	0.695	−1.28	has been used
1500	0.7300	0.715	−2.05	0.717	−1.79	
2000	0.7468	0.734	−1.71	0.738	−1.18	2. In formula (13) the
2500	0.7630	0.751	−1.57	0.755	−1.05	individual exponent
3000	0.7774	0.765	−1.59	0.770	−0.95	$q = 2.832$ is taken
3500	0.7910	0.778	−1.64	0.784	−0.88	according to the da-
4000	0.7996	0.790	−1.20	0.797	−0.33	ta from the tables
4500	0.8110	0.801	−1.23	0.808	−0.37	of Landolt-Börnstein
5000	0.8195	0.811	−1.04	0.819	−0.06	
5500	0.8300	0.821	−1.08	0.829	−0.12	3. Tabulated values of
6000	0.8385	0.829	−1.13	0.839	+0.06	the density are the
7000	0.8535	0.845	−1.00	0.856	+0.29	average value of
8000	0.8669	0.860	−0.80	0.871	+0.47	the measurements
						by Bielinski and
						Bridgeman

([3]) The average value for liquid n-paraffins from C_5 to C_{16} is 2.941, whereas the average value for a series of homological paraffins, olefins as well as aromatic hydrocarbons is $q = 2.963$ [13].

Table 4. Calculations of

Δp [bar]	ϱ_{table}	n-heptane $\varrho_{calculated}$ [g/cm³]	Deviation [%]	Remarks
0	0.6753	—	—	For the calculations the exponent
50	0.6803	0.6793	−0.15	$q = 2.953$ is taken according to Landolt's
100	0.6849	0.6831	−0.26	table $w = 1113 \left[\dfrac{m}{s} \right]$
200	0.6933	0.6904	−0.42	
300	0.7010	0.6973	−0.53	$\dfrac{dw}{dT} = -4.14 \left[\dfrac{m}{s\,deg} \right]$
500	0.7142	0.7100	−0.59	
1000	0.7406	0.7369	−0.50	$\alpha = 12.60 \cdot 10^{-4}$ [deg⁻¹] for a tempe-
1500	0.7612	0.7590	−0.29	rature $+30°C$. The values of density are
2000	0.7783	0.7738	−0.06	from Wargaftik [12].
3000	0.8063	0.8090	+0.34	
5000	0.8480	0.8558	+0.92	

It can be seen from Table 3 that better agreement with the experiment is obtained by using the individual exponent q in formula (13), than — the universal exponent $q = 3$ in formula (13a). In further calculations the former will thus be used.

Obviously, in the first approximation it is possible by using the universal exponent $q = 3$, to determine the liquid density at higher pressures with an accuracy of 2-3 %, and this requires knowlegde of the liquid density and the sound velocity for only one measuring point, e.g. at room temperature and normal pressure.

It should be added that even better agreement of the experimental results with the values of the densities calculated on the basis of formula (13) can be obtained with the aid of experimental data on the liquid density and sound velocity at a higher pressure than that of the normal pressure (13).

As an example, assuming as initial data for the calculations for diethyl ether at a pressure of $p = 500$ atm $\varrho = 0.7615$ g/cm³ (from BRIDGEMAN [11]), and $w = 1284$ m/s (according to RICHARDSON and TAIT [10]), then the average deviation of the results of the values of the densities calculated from experimental data obtained by BRIDGEMAN [11] in the pressure range from 1000 to 12 000 atm is ± 0.25 %, compared to a deviation of ± 0.69 % for initial data taken at normal pressure. Thus, it is possible in some cases to extrapolate the results obtained at not too high pressures to considerably higher pressure ranges.

5. Results

The value of the so called Rao expression at constant temperature is almost independent of the pressure, as was pointed out by SCHAAFFS. In this paper it

density of n-heptane and diethyl ether

p [atm]	ϱ table [g/cm³]	Diethyl ether ϱ calculated [g/cm³]	Deviation [%]	Remarks
1	0.7138	—	—	
500	0.7615	0.755	−0.88	For the calculations the exponent value
1000	0.7885	0.786	−0.30	$q = 2.840$ has been taken according to
1500	0.8117	0.8116	−0.01	Landolts'table
2000	0.8319	0.833	+0.16	$w = 1006$ [m/s]
2500	0.8498	0.852	+0.27	$\dfrac{dw}{dT} = 4.66$ [m/s deg]
3000	0.8658	0.869	+0.35	$a = 16.31 \quad 10^{-4}$ [deg⁻¹]
3500	0.8800	0.884	+0.45	$t = 20°C$
4000	0.8928	0.898	+0.55	
4500	0.9045	0.910	+0.64	
5000	0.9152	0.922	+0.75	
6000	0.9339	0.943	+0.99	Density data are taken from **Brid-**
7000	0.9508	0.962	+1.18	**geman's** papers [11]
8000	0.9670	0.979	+1.23	
9000	0.9826	0.994	+1.19	
10000	0.9976	1.008	+1.09	
11000	1.0120	1.022	+0.95	
12000	1.0256	1.034	+0.80	

has been shown that a somewhat better stability of this expression is obtained by using individual liquid exponents and an attempt has been made to prove this fact theoretically.

From this a relation has been obtained from which it is possible to determine the pressure dependence of the liquid density over a broad pressure interval. This method is very simple since it requires only the knowledge of changes in density and sound velocity as a function of temperature at normal pressure and gives better agreement of the calculated densities with experimental values than do the majority of known methods.

References

[1] J. WEHR, *An ultrasonic method for the determination of the compressibility of a liquid as a function of pressure*, IPPT Reports 15/1967 [in Polish].

[2] W. SZACHNOWSKI, *An ultrasonic method for measuring the compressibility of liquid fuels and hydraulic and lubricating liquids as a function of pressure and temperature*, Doctoral thesis, IPPT PAN, Warszawa 1973 [in Polish].

[3] W. SCHAAFFS, *Molekularakustische Abteilung einer Zustandsgleichung für Flüssigkeiten*, Acustica, **30** (1974).

[4] K. WOŹNICZAK, *Sound velocity versus the latent heat of vapourization*, Archiwum Akustyki, **7**, 3-4, 319-325 (1972)[inPolish].

[5] E. Soczkiewicz, *The relationship of the velocity of ultrasound in liquids to the pressure in terms of the intermolecular potential*, Science Textbook of the Śląsk Polytechnic Mathematics-Physics, **25**, 47-57 (1974) [in Polish].

[6] E. Soczkiewicz, *The generalized Lennard-Jones potential and the acoustical properties of liquids*, Doctoral thesis, IPPT PAN, Warszawa 1973 [in Polish].

[7] B.A. Bielinskij, Sz. Ch. Ikramow, *Kompleksnoje issliedowanije akusticzeskich parametrow wiazkosti i plotnosti n-pentana w szirokom intervale dowleniji*, Akust. Żurnał, **18**, 355-359 (1972).

[8] E. Grüneisen, *Über die Theorie des einatomiger Festkörper*, Annalem der Physik, **39**, 257-306 (1912).

[9] J.G. Kirkwood, H. Bethe, *Office of Scientific Research and Development*, Rep. 588, 1942.

[10] E.G. Richardson, R. I. Tait, *Rations of specific heat and high-frequency viscosities in organic liquids under pressure*, Philosophical Magazine, **2**, 441-454 (1957).

[11] P.W. Bridgeman, *Colected experimental papers*, V. I, 486, Cambridge 1964.

[12] N.B. Wargaftik, *Sprawocznik po tieplofiziczeskim swojstwam gazow i żidkostiej*, Moskwa 1972, s. 266.

[13] From the author's calculations (unpublished).