

Density Measurement of Fluids with a Vibrating Densimeter at several Temperatures

Reiji Tanaka*

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The ability of a vibrating densimeter developed by Picker *et al.* was examined for fluids including nitrogen gas, water, and organic liquids at 298.15 K, 299.15 K, and 303.15 K. The relationship for vibration period vs. liquid density could be verified to be linear consistently for the investigated fluids at a fixed temperature.

Introduction

The density of liquids is obtained commonly by pycnometry or float technique. The drawbacks in those methods are that a relatively large amount of sample liquid is used, and the technical process is rather complicated. Also the accuracy of measurement may be sacrificed in the volume determination of organic mixtures since the concentration is easily changed by evaporation while the mixture is introduced into the cell. Recently, on the other hand, an elegant method has been developed as a digital densimeter, the principle of which is based on the measurement of resonant frequency of the cell tube filled with the sample fluid. Some instruments are commercially available at present. The ability of this new method, however, has not been verified well, still being left with the hope of settling the drawbacks in the former ways. An Anton Parr densimeter has been tested against organic liquids by Kiyohara *et al.* and a shortcoming of this instrument was indicated.¹⁾ Another one commercially available is developed by Picker *et al.* The latter has been tested precisely on aqueous electrolyte solutions,²⁾ and also applied especially for highly dilute concentrations verifying the excellent efficiency.³⁾ However, over all test including organic liquids has not been achieved yet with this instrument. Further test and experience with this type of instrument is considered to

be very important. Therefore, this note reports results of examination for a digital densimeter (Vibrating Densimeter Model 01D, manufactured by Sodev Inc., Canada) on fluids including nitrogen gas, water, and fourteen organic liquids at 298.15K, 299.15K, and 303.15K.

Density measurement by pycnometry

In the vibrating densimeter, the density ρ of fluid which is fed in the cell tube is generally related to the resonant period T with constants A and B as follows:

$$\rho = A + BT^2 \quad (1)$$

The two constants of this equation are determined by calibration from the known ρ and corresponding T using more than two fluids. In order to examine the relationship (1) fourteen organic liquids were chosen, and their densities were measured with an Ostwald pycnometer. The volume of pycnometer (ca. 50cm³) was determined with pure water distilled from KMnO₄ solution. The density values of water taken as standard were 0.997047 g cm⁻³, 0.996786 g cm⁻³, and 0.995650 g cm⁻³ at 298.15K, 299.15K, and 303.15K respectively.⁴⁾ The temperature θ of the water bath, which was monitored by a quartz thermometer (Hewlett Packard, 2801A), was regulated within ± 0.001 K, and the accuracy was estimated to be about ± 0.01 K at the examined temperatures.

The organic samples were not treated chemically

* Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto-cho, Sumiyosi-ku, Osaka, 558 Japan.

at all, but so that the liquids were saturated with air the bottles were shaken well before the density measurements. This process was rather important to avoid a gradual change of ρ due to absorption of air. All weights were corrected to *vacuo* with the calculated density of air as a function of temperature, pressure, and relative humidity.⁵⁾ The densities of sample liquid determined by pycnometer, ρ_p are shown in Table 1: each measurement was carried out at least twice to make certain of the operation. The error in pycnometry was attributed to uncertainties in the balance weights, in the temperature of measurements, and in the estimation of air density, and to the repeatability of weighing the liquid fed in the pycnometer. The total error accompanied in the volume determination of the pycnometer was assigned to the systematical one. The error sources in the weight measurement of sample liquids were assigned into either the systematic or the random one, but in some cases the classification was somewhat obscure. Among those, primary sources of error were in the air density and the absolute temperature value. The possible limit of systematic error was estimated to be $(0.000014 \text{ g cm}^{-3} + 0.000028 \rho)$, and the random one was about $\pm 0.000008 \text{ g cm}^{-3}$ for organic liquids. The density of dry nitrogen gas was calculated from the ideal gas law.

Test on the vibrating densimeter

The temperature of the densimeter was controlled by circulating water which was supplied from the same bath as used for the pycnometry with the use of a gear pump (Variable Speed Gear Pump Model 12-41-316, Micro Pump Corp., U.S.A.) at a flow rate of ca. 2.5 liter per min. The stability of the temperature was $\pm 0.002 \text{ K}$. The resonant period was measured by a digital frequency counter (Newport Model 700, U.S.A.) with eight digits which were renewed each 3 s under 10^3 integration. Usual unstability of each reading was within $\pm 0.002 \mu\text{s}$. In order to omit erroneously counted values, the average was taken manually. For the density calculation the period averaged for 40 readings was used. In all cases the cell tube was first cleaned with a few cm^3 of acetone, then ether, and finally dried up with nitrogen gas for 5 min before a sample was flowed in. A testing run was

kept on for 60 min, and the same observations were repeated successively. Though a flow (dynamic) mode with partially degassed liquid is recommended in the operation manual, the present test were carried out under stopped flow (static) mode with liquids saturated with air, since it was found that the degassed liquids revealed a significant gap or drift of T due to the change of density while the sample was exposed to the air.

The most important requirement in the densimeter is the stability and the reproducibility of T counted on a fluid rather than the linearity in equation (1). The test was started after aging the oscillator with the power switch on for a year. The most recent aspects of T change against time t observed for hexane are illustrated in Fig. 1, in which a mark represents an average for 10 readings. As shown in the figure it takes 20–30 min to reach equilibrium of T in the case of organic liquids, and stays constant with a scattering of $\pm 0.001 \mu\text{s}$ which corresponds to a precision of $\pm 3 \times 10^{-6} \text{ g cm}^{-3}$ in density. The drift of T after equilibrium was not significant during 4 h in this case, but a

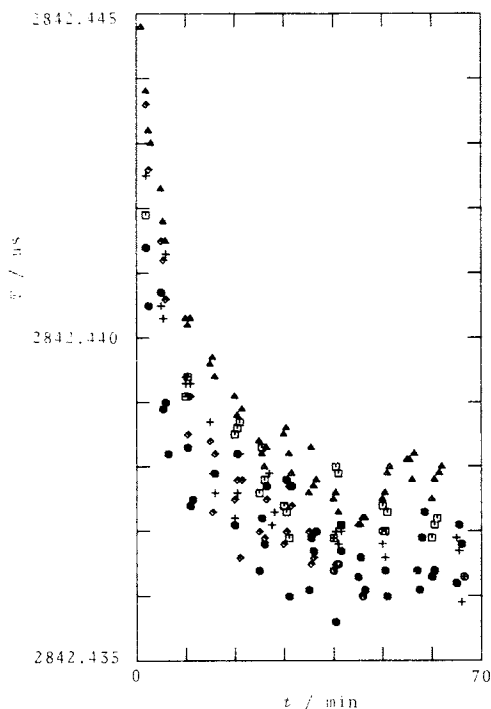


Fig. 1. Testing runs for the drift of T using hexane with static mode: they are measured successively in the order of \blacktriangle , $+$, \square , \blacklozenge , and \bullet ; \bullet , run of the next day.

small drift of 0.001 μ s per h has been often observed, but also, an increase in drift has occasionally occurred. The equilibrium period for water is 2 h but is much shorter for gas, about 5 min. When a liquid of a similar density is fed successively, the counting reaches equilibrium much more quickly.

Dynamic method with a flow of 1 cm³ per min failed to reveal a significant difference on the readings.

In Table 1, the comparison between the densities obtained by the pycnometry ρ_p , and those by the densimeter ρ_v , are shown. The constants required

Table 1 Comparison of density measurements

Liquid	$\rho_p/g\text{ cm}^{-3}$	$\rho_v/g\text{ cm}^{-3}$	$\Delta\rho/g\text{ cm}^{-3}$	$\rho_p/g\text{ cm}^{-3}$	$\Delta\rho/g\text{ cm}^{-3}$
At $\theta = 298.15\text{ K}$					
		Determined by least squares method		Determined by C ₆ H ₁₄ and CCl ₄	
N ₂ gas	0.001145	0.001144	-0.000001	0.001136	-0.000009
Hexane	0.656214	0.656215	0.000001	0.656214	0.000000
Heptane	0.679870	0.679863	-0.000007	0.679862	-0.000008
2,2,4-Trimethylpentane	0.687733	0.687739	0.000006	0.687738	0.000005
Methylcyclohexane	0.765037	0.765043	0.000006	0.765043	0.000006
Propanol	0.799666	0.799678	0.000012	0.799679	0.000013
Toluene	0.862221	0.862219	-0.000002	0.862219	-0.000002
Benzene	0.873650	0.873649	-0.000001	0.873650	0.000000
Styrene	0.901925	0.901921	-0.000004	0.901922	-0.000003
Cyclohexanone	0.942186	0.942186	0.000000	0.942188	0.000002
Water	0.997047**	0.997033	-0.000014	0.997035	-0.000012
Benzonitrile	1.000104	1.000092	-0.000012	1.000094	-0.000010
Chlorobenzene	1.101076	1.101077	0.000001	1.101080	0.000004
Nitrobenzene	1.198168	1.198175	0.000007	1.198179	0.000011
<i>o</i> -Dichlorobenzene	1.300475	1.300489	0.000014	1.300494	0.000019
Tetrachloromethane	1.584233	1.584226	-0.000007	1.584233	0.000000
		$\sigma(g\text{ cm}^{-3}) = 0.000008$		$\sigma(g\text{ cm}^{-3}) = 0.000008$	
		A* = -5.357516		A = -5.357572	
		B* = 744329.05		B = 744335.75	
At $\theta = 299.15\text{ K}$					
N ₂ gas	0.001141	0.001143	0.000002	0.001186	0.000045
Hexane	0.655337	0.655308	-0.000029	0.655337	0.000000
Water	0.996786**	0.996847	0.000061	0.996869	0.000083
Chlorobenzene	1.100017	1.099995	-0.000022	1.100015	-0.000002
Tetrachloromethane	1.582318	1.582308	-0.000010	1.582318	0.000000
		$\sigma(g\text{ cm}^{-3}) = 0.000035$		$\sigma(g\text{ cm}^{-3}) = 0.000047$	
		A = -5.357364		A = -5.357211	
		B = 743983.38		B = 743968.04	
At $\theta = 303.15\text{ K}$					
N ₂ gas	0.001126	0.001115	-0.000011	0.001131	0.000005
Hexane	0.651693	0.651671	-0.000022	0.651693	0.000000
Water	0.995650**	0.995736	0.000086	0.995761	0.000111
Chlorobenzene	1.095717	1.095691	-0.000026	1.095717	0.000000
Tetrachloromethane	1.574554	1.574527	-0.000027	1.574554	0.000000
		$\sigma(g\text{ cm}^{-3}) = 0.000048$		$\sigma(g\text{ cm}^{-3}) = 0.000056$	
		A = -5.356263		A = -5.356300	
		B = 742521.32		B = 742528.54	

* Units: A, g cm⁻³; B, g cm⁻³ s⁻².

** Standard value taken from the reference (4).

for the latter were determined by two ways: least squares calculation referring to all liquids, and simple calculation on the two liquids, hexane and tetrachloromethane. Those densities are listed along with the constants, A and B, and the standard deviation σ . The calculated densities according to equation (1) are in reasonable agreement at 298.15 K with those obtained by the pycnometry considering the experimental error described above. However, it must be noted that the present agreement was secured by adjusting the value of current which drives the magnetic oscillator from original 0.63 mA to 0.87 mA since in the original model, water failed to align on the relationship (1) of T^2 vs. ρ_p by an amount of $1 \times 10^{-4} \text{ g cm}^{-3}$.*

In order to check the efficiency at different temperatures, similar measurements were also carried out at 299.15 K and 303.15 K. This test becomes necessary for the examination of thermal expansion of fluids. At these temperatures the agreement is again good except for water. The deviation for nitrogen gas is probably due to the relatively poor reproducibility of T which depends on the delicate change of measurement condition. The disagreement for water at those temperatures, which is obviously larger than experimental error, means that the driving power of oscillator must be re-adjusted for a changed temperature when aqueous systems are interested. The listed results suggest that the constants A and B may be determined with two liquids instead of the least squares method. However, nitrogen gas and water are not suited for this purpose since the T of the former changes delicately as mentioned above, and the latter consumes period for the equilibrium, up to

2 h.

The temperature dependence of calibration constants can be estimated from the obtained constants: $(\partial A/\partial \theta) \approx 0.000251 \text{ g cm}^{-3} \text{ K}^{-1}$, and $(\partial B/\partial \theta) \approx 361.5 \text{ g cm}^{-3} \text{ s}^{-2} \text{ K}^{-1}$. An increase of temperature, after a cancellation between those gradients of the constants and the thermal expansion of fluid, causes an increase of T by $0.5 \mu\text{s}$ per degree. Therefore the correction for the temperature deviation must be done carefully and also the calibration must be renewed for each temperature to be changed.

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* Similar trouble was also experienced for the same model by a different laboratory.⁶⁾