A New Method for Measuring Fluid Densities Using the Taylor Dispersion Experiment

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The density of a pure fluid or a fluid mixture is of fundamental importance in the design of equipment for fluid processing and in the development of theory describing thermodynamic and transport properties of the liquid state. A new experimental technique for measuring fluid densities is presented, which is based on the well-known Taylor dispersion experiment for measuring mutual diffusion coefficients. The equipment and working equation are both simple, yet experimental results show that the method is accurate to at least 0.1%. An analysis of errors indicates that the accuracy could be improved to 0.01%. This new technique is of particular virtue since it can be used to obtain simultaneous measurements of the fluid density and diffusion coefficient of a solute in the fluid, using data from a single experiment.

1. INTRODUCTION

A number of experimental techniques are used to measure the pressure–volume–temperature relationships of pure fluids and fluid mixtures. Among the techniques are the oscillating u-tube, the Burnett method, the buoyancy force technique, and the pycnometer. These have their own advantages and disadvatages; in particular, construction and operation are expensive and difficult at high temperatures and pressures.

We developed a new technique for measuring fluid densities. The technique is based on the Taylor dispersion experiment for measuring mutual diffusion coefficients in Newtonian fluids. The design equations are presented, along with confirming experimental data. The preliminary

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experimental results indicate the method to be accurate to at least
$\pm 0.05\%$, and we describe the refinements necessary for obtaining even
greater accuracies. Thus, this new technique should be competitive with
other established methods. An analysis of errors is given along with advan-
tages and disadvantages of the method. Two notable features of this
method are that the apparatus can be constructed entirely from commer-
cially available chromatography equipment and that simultaneous
measurements of density and diffusivity can be made.

2. THEORY OF EXPERIMENT

If a narrow pulse of a solute is injected into a long narrow tube, in
which a Newtonian solvent is moving in slow laminar flow, then the initial
narrow pulse will disperse due to the combined effects of bulk flow and
molecular diffusion. Under the proper conditions, the solute concentration
profile will eventually become normal, and the center of gravity of the
profile will move with the mean velocity $\bar{u}$ of the laminar flow. This
phenomenon is called Taylor dispersion after G. I. Taylor, who provided
the first mathematical explanation [1]. Aris [2] subsequently provided a
more thorough treatment. Alizadeh et al. [3] recently presented a detailed
review of theory and criteria for designing a Taylor dispersion apparatus
for measuring mutual diffusion coefficients. We follow the work of Alizadeh
et al. but present here only those results necessary for determining density.

If the concentration profile $C(t)$ at the end of the dispersion tube is
measured as a function of time t, then one can calculate this first three tem-
poral moments as follows:

$$M = \int_0^t C(t)\, dt$$

$$\bar{t} = \frac{1}{M} \int_0^t t C(t)\, dt \tag{1}$$

$$\sigma^2 = \frac{1}{M} \int_0^t (t - \bar{t})^2\, C(t)\, dt$$

M is the sum or material balance function; $\bar{t}$ is the normalized first
moment or center of gravity and represents the time at which the center of
the peak leaves the dispersion tube. σ^2 is the normalized, centralized tem-
poral variance.

The key to density measurement is the fact that the center of gravity
moves with the mean speed of flow. It can be shown [4, 5] that

$$\bar{t} = \frac{L}{\bar{u}} (1 + 2\zeta_0) \tag{2}$$

where L is the tube length and ζ_0 can be calculated from [3]

$$\zeta_0 = \frac{2\sigma^2 - \bar{t}^2 + [\bar{t}^4 + 4\bar{t}^2\sigma^2]^{1/2}}{[8\bar{t}^2 - 4\sigma^2]} \tag{3}$$

Thus, $\bar{t}$ can be calculated from Eq. (1), and if L is known, $\bar{u}$ can be calculated from Eq. (2).

Now consider a mass balance over the diffusion tube of length L and radius R. At steady state, the mass flow rate $\dot{m}$ is constant:

$$\dot{m} = \pi R^2 \bar{u}\rho = \pi R^2 \left[\frac{L}{\bar{t}} (1 + 2\zeta_0) \right] \rho \tag{4}$$

where ρ is the fluid density. If one performs the Taylor dispersion experiment at a known mass flow rate, then ρ can be calculated directly from Eq. (4) if L and R are known.

There is an alternative method of calculating density which is preferred. Since L is typically tens of meters and R is typically fractions of a centimeter, these quantities are rather difficult to measure accurately. Consider instead performing the experiment twice, first at condition 1 using a fluid of known density ρ_1, then at condition 2 where ρ_2 is unknown. In general, condition 2 is at a different temperature, pressure, and flow rate, with a different fluid. We may write Eq. (4) for both experiments and solve for ρ_2 as a ratio to the known density:

$$\frac{\rho_2}{\rho_1} = \frac{\bar{t}_2}{\bar{t}_1} \frac{\dot{m}_2}{\dot{m}_1} \frac{(R^2L)_1}{(R^2L)_2} \frac{(1 + 2\zeta_0)_1}{(1 + 2\zeta_0)_2} \tag{5}$$

In Eq. (5) the radius and length at conditions 1 and 2 are not generally the same due to thermal expansion and pressure effects. However, these effects are small and can be accurately accounted for using standard equations of mechanics. Thus, rather than measuring R_1, R_2, L_1, and L_2, one computes the volume ratio $(R^2/L)_2/(R^2L)_1$, which involves only temperature and pressure correction terms. We emphasize that only a single reference experiment 1 need be performed, from which the density of any other fluid may be calculated.

3. VERIFICATION OF THEORY

3.1. Apparatus

The Taylor dispersion apparatus used to make density measurements is shown in Fig. 1. This apparatus was designed primarily for measuring diffusion coefficients in hydrocarbon systems [6].

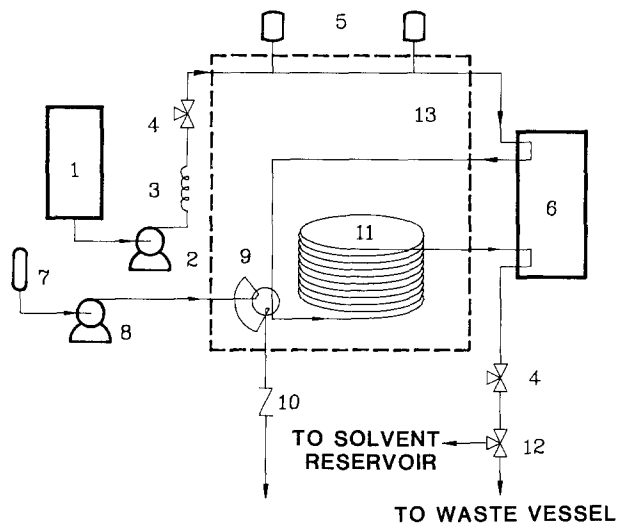Initially the solvent is sparged with helium to remove air, and then a

Fig. 1. Schematic diagram of high-pressure, high-temperature Taylor dispersion apparatus. (1) Solvent reservoir. (2) Solvent pump. (3) Capillary tubing pulse dampener. (4) Back-pressure regulators. (5) Pressure transducers. (6) Refractive index detector. (7) Sample solution. (8) Sample injection pump. (9) Six-port sample injection valve. (10) Adjustable check valve. (11) Coiled dispersion tube. (12) Three-way valve. (13) Heated enclosure.

helium blanket is maintained on the solvent reservoir. The solvent pump is an LDC/Milton Roy Constametric III with the slow-speed option. Flow rates are typically 0.1 to 0.2 ml · min^{-1}. The solvent is pumped through 3.05 m of 0.0254-cm-i.d. capillary tubing and then through a Grove back-pressure regulator set at 145 kN · m^{-2}. The back-pressure regulator and capillary tube serve to damp out pressure pulses from the pump. Pressure in the system downstream of the pulse dampener is maintained by a second Grove regulator located at the outlet.

Two calibrated strain-gauge pressure transducers (Teledyne Taber Model 2201) are used to measure the pressure of the experiment. After passing the transducers, the solvent flows out of the heated enclosure to the reference cell of an LDC/Milton Roy Refractomonitor III differential refractive index detector. The temperature in the detector cell is maintained at 313 K by a Fisher Model 80 circulating water bath. The solvent then flows from the detector reference cell back to the heated enclosure, in which a six-port chromatographic sample injection valve (Valco A6C6WT) is located. The sample solution is prepared external to the heated enclosure and pumped into the sample loop. Pressure on the sample loop is maintained at the experimental pressure with an adjustable check valve.

The solute pulse next flows to the diffusion coil. The dispersed solute peak leaves the heated enclosure and flows through the sample cell of the detector, then through the second backpressure regulator. During experiments, the eluting solute/solvent mixture is collected and discarded. At other times, the solvent is recirculated directly back to the solvent reservoir so that the pump can be left on continuously.

The heated enclosure is constructed from aluminum pipe whose ends are covered with aluminum plate. The diffusion tube is coiled on an aluminum ring which fits snugly inside the pipe. The void space inside the enclosure is filled with aluminum shot so that the system is thermally massive and stable, with good internal heat conduction.

Two Commodore B-128 personal computers are used for data logging and as controllers. One computer is dedicated to on-line monitoring of the detector signal. The signal is recorded every 5 s, giving at least 200 time/concentration points for each response curve. The second computer is used for monitoring pressure and temperature and also for controlling the temperature in the enclosure.

As discussed by Alizadeh et al. [3], the moments $\bar{t}$ and σ^2 in Eqs. (1)–(5) are those which would be measured if there were no imperfections in the apparatus. In reality, one must deal with the nonzero volume of the concentration detector, the nonzero width of the injection pulse, and an additional length of tubing needed to connect the dispersion tube to the detector. Corrections $\delta \bar{t}_i$ and $\delta \sigma_i^2$ to the actual observed moments $\bar{t}_{\mathrm{obs}}$ and σ_{obs}^2 are given in Ref. 3 and are applied as follows:

$$\bar{t} = \bar{t}_{\mathrm{obs}} + \sum \delta \bar{t}_i$$

$$\sigma^2 = \sigma_{\mathrm{obs}}^2 + \sum \delta \sigma_i^2$$

(6)

To correct for the nonzero volume V_{D} of the detector:

$$\delta \bar{t}_1 = -\left(\frac{L}{\bar{u}}\right)\left(3\zeta_0 - \frac{V_{\mathrm{D}}}{\pi R^2 L}\right)$$

$$\delta \sigma_1^2 = -\left(\frac{L}{\bar{u}}\right)^2 \left[13\zeta_0 - \left(\frac{V_{\mathrm{D}}}{\pi R^2 L}\right)^2 - 2\zeta_0\left(\frac{V_{\mathrm{D}}}{\pi R^2 L}\right)\right]$$

(7)

To correct for the nonzero volume V_i of the injection pulse:

$$\delta \bar{t}_2 = -\left(\frac{L}{\bar{u}}\right)\left(\frac{V_i}{2\pi R^2 L}\right)$$

$$\delta \sigma_2^2 = -\left(\frac{1}{12}\right)\left(\frac{L}{\bar{u}}\right)^2 \left(\frac{V_i}{\pi R^2 L}\right)^2$$

(8)

To correct for the additional length of tubing L_c needed to connect the diffusion coil to the detector:

$$\delta \bar{t}_3 = -\left(\frac{L_c}{\bar{u}}\right)\left(\frac{R_c}{R}\right)^2\left[1+\left(\frac{L}{L_c}\right)\zeta_0\left(1+\frac{R_c{}^2}{R^2}\right)\right]$$

$$\delta \sigma_3^2 = -\left(\frac{L_c}{\bar{u}}\right)^2\left(\frac{R_c}{R}\right)^4\left[\left(\frac{L}{L_c}\right)\zeta_0+\frac{R_c^2}{R^2}\left(\frac{L}{L_c}\right)^2\zeta_0^2\left(\frac{3R_c{}^2}{R^2}\right)+2\right]$$

(9)

where R_c is the radius of the connecting tube.

For density, the most important quantity is $\bar{t}$, which can be estimated to better than 0.05%. In our work, we calculate $\bar{t}_{obs}$ and σ_{obs}^2 by finite summation approximations to Eqs. (1).

3.2. Density Measurements

Distilled, deionized water was used as the calibration fluid, since very accurate density data are available for a wide range of temperatures and pressures [7]. We performed two calibrations ($T = 303.2$ K, $P = 8.24$ kN · m^{-2} and $T = 303.0$ K, $P = 9.33$ kN · m^{-2}). The values of $\dot{m}$, $\bar{t}$, ρ, and ζ_0 for the calibrations are given in Table I. In the calibration experiments, a 2 wt% methanol solution in water was used as the tracer.

The Taylor dispersion experiment was then performed at temperatures of 329, 354, and 393 K. Two experiments were done at each temperature, one using methanol as tracer and one using isopropanol. The tube volume was corrected for temperature effects using the thermal expansion coefficient α for austenitic stainless steels [8].

$$\frac{(R^2L)_1}{(R^2L)_2} = (1 + \alpha \Delta T)^{-3}$$

(10)

Table I. Calibration Data Using Water as the Reference Fluid

	Calibration No.	
Quantity	1	2
$\dot{m}$	0.17762	0.17750
$\bar{t}$ (s)	12,517	12,518
T (K)	303.2	303.0
P (kN · m^{-2})	392	396
ζ_0	1.736×10^{-4}	1.844×10^{-4}
ρ (g · cm^{-3})	0.995785	0.99579

Table II gives the calculated and literature values of water density. The agreement with literature values is excellent, the average absolute deviation being 0.025 %. The slightly larger errors at 392 K may be due to small thermal gradients within our apparatus, which limit the accuracy of temperature measurement.

   The method was further demonstrated by measuring the density of a hydrocarbon, n-dodecane, as a function of temperature and pressure. In this case, both n-tetradecane and n-octane were used as tracers, and the density was calculated from Eq. (5) using the same water calibration data as the reference. The comparison with true densities is given in Table II. True densities up to 483 K were calculated with the data from Ref. 9. The agreement again is good, although the errors are somewhat larger than those for water. The lack of agreement is explained in part by error in interpolation, which is required to use the density correlations of Ref. 9. These errors were said to be of the order of $0.0008 \text{ g} \cdot \text{cm}^{-3}$.

Table II. Calculated Densities of Pure Water and Pure n-Dodecane

Tracer[a]	T (K)	P (kN·m^{-2})	$\dot{m}$ (g·min^{-1})	$\bar{t}$ (s)	$10^4 \rho_0$	ρ^b (calc.) (g·cm^{-3})	ρ (lit.) (g·cm^{-3})	Error (%)
				Water				
M	330	396	0.17686	12,451	2.05	0.98523	0.98512	+0.01
P	329	396	0.17660	12,468	1.05	0.98534	0.98522	+0.01
M	354	396	0.17503	12,412	0.75	0.97103	0.97125	−0.02
P	354	394	0.17563	12,373	1.4	0.97117	0.97125	−0.008
M	392	394	0.16900	12,513	0.50	0.94342	0.94397	−0.06
P	393	394	0.16840	12,559	0.80	0.94344	0.94341	+0.003
				n-Dodecane				
C8	304	1393	0.12910	12,836	3.25	0.7422	0.7421	0.01
C14	373	1412	0.13133	11,796	2.24	0.6916	0.6921	−0.07
C8	373	3443	0.13008	11,930	1.42	0.6929	0.6937	−0.11
C8	443	1446	0.13102	10,923	1.71	0.6366	0.6372	−0.09
C8	444	3454	0.13117	10,959	0.81	0.6396	0.6409	−0.20
C8	515	3436	0.13101	10,020	0.52	0.5818	—	—
C14	513	1451	0.13059	9,969	0.81	0.5780	—	—
C14	567	1456	0.13148	8,961	0.57	0.5231	—	—
C8	567	3438	0.13195	9,119	0.39	0.5318	—	—

[a] M, methanol; P, isopropanol; C8, n-octane; C14, n-tetradecane.
[b] Density is calculated twice from Eq. (5), using the two calibration points. These values are averaged to give the value in the table.

4. DISCUSSION

4.1. Error Analysis

As stated earlier, the present apparatus was designed for measuring diffusion coefficients, and thus no particular preparation was made for measuring density. Even so, we have shown that a very good measurement may be obtained with little effort. In this section we discuss sources of error and improvements which could be made to increase precision.

4.1.1. Temperature

In our apparatus, temperature measurement is made with several calibrated thermistors, with an estimated accuracy of $\pm 0.1\ K$ for an individual thermistor. However, small temperature gradients exist within the heated enclosure and our reported temperatures are averages with an estimated precision of ± 1 K. For water, an uncertainty in temperature of ± 0.5 K at 393 K and 390 kN $\cdot$ m^{-2} corresponds to an uncertainty in density of about ± 0.00040 g $\cdot$ cm^{-3}, or about $\pm 0.05\%$. Thus, uncertainty in our temperature measurement likely accounts for much of the error in density in Table II. For measurements of liquid densities accurate to 0.00001 g $\cdot$ cm^{-3}, temperature accuracy of the order of 0.005 K would be needed. This can be achieved using alternate methods of temperature measurement and construction of a more temperature environment.

4.1.2. System Volume

In our calculations, we accounted for thermal expansion of the diffusion tube by using handbook values of the thermal expansion coefficient [8]. The term $(1 + \alpha \varDelta T)^3$ was 1.00451 at 392 K, or change in the volume of tubing required a correction factor of about 0.45%. We neglected any pressure corrections at our conditions, but obviously the correction to volume increases with pressure and temperature. For extremely precise work, it would be preferable to calibrate the tube volume as a function of temperature and pressure. This could be done by performing the Taylor dispersion experiment using water as the calibration fluid over the desired range of conditions.

4.1.3. The Tracer

Since the Taylor dispersion experiment requires introducing a trace of solute in the flowing solvent, the composition of liquid within the diffusion

tube is nonuniform. In principle, then, the density is not that of the pure solvent but of the solvent plus solute. However, modern chromatographic equipment can detect very low concentrations, so in practice the error introduced is slight. In our experiments with water, the solute was either methanol or isopropanol at 2 wt%. A 50-μl pulse was injected into the diffusion tube, whose volume was nearly 40 ml. Thus the tracer accounted for roughly 0.03% of the material within the dispersion tube. Although the pure component densities of the alcohols are appreciably lower than that of water, this had no observable effect on the density measurement. If desired, any error due to the tracer could be further reduced by using a solute of the same density or by using an isotopic tracer.

4.1.4. Mass Flow Rate

The flow rate is best measured by averaging the total mass of solvent collected by the time of experiment. In this way, small fluctuations in flow are averaged out. The time of our experiments is typically 10,800 s, measured to ± 0.1 s. The collected mass was of the order of 37 g, ± 0.003 g. Thus mass flow rate was measured to about $\pm 0.01\%$.

4.1.5. Center of Gravity

In our work, calculation of the center of gravity $\bar{t}$ has an estimated uncertainty of ± 5 s of a total of about 10,800 s (0.05%). Alternative methods of calculating $\bar{t}$, such as graphical or numerical fitting of the data, would not improve the accuracy noticeably. Thus the value of $\bar{t}$ to be used in Eq. (5) is the limiting factor in the accuracy of the method. However, with multiple experiments one can increase the accuracy of the measurement by using an average value of $\bar{t}$. This is easily done if one wishes to obtain the mutual diffusion coefficient also, because it is typical to perform three or more replicate Taylor diffusion experiments and report the average diffusion coefficients. Thus replicate density data can be obtained simultaneously.

To summarize, a theoretical analysis of error in our experiment indicates a total uncertainty of about $\pm 0.1\%$ in density. Our experimental results with water show an average uncertainty of only 0.025%, which indicates that the error analysis is conservatively high. By refining the technique as described above, an ultimate accuracy of 0.01% should be feasible.

4.2. Application of the Method

The experimental principles apply to either liquids or gases. One needs only to meet the criteria for the Taylor dispersion analysis to hold [3]. The most serious restriction with regard to density measurements is that the fluid be Newtonian, so that the laminar parabolic velocity profile be established. Even this requirement can be relaxed for certain non-Newtonian fluids if stress-induced diffusion is negligible [10].

In addition to a very good accuracy, this method has two distinct advantages. First, the equipment needed is the same as used in liquid or gas chromatography (pumps or mass flow controllers, detector, tubing, sample injection equipment) and thus is commercially available. The need for specialized and expensive equipment construction is bypassed.

Second, the diffusion coefficient of the solute tracer may be determined simultaneously. Since some theoretical treatments of diffusion coefficient require knowledge of the solvent molar volume, the density data would be valuable. The Taylor dispersion method has been applied at elevated temperatures and pressures [11] and using binary mixtures as solvent [12]. For mixtures at high temperatures and pressures, accurate density data are scarce. Having the capability of measuring density and diffusivity simultaneously in such mixtures would greatly speed data acquisition and thus theoretical development.

There are also limitations to this method. First, there will be a small pressure drop along the diffusion tube. Although this will be negligible most of the time, the effect on density will be large near the critical point. Therefore, near the critical point a static method would be needed rather than the dynamic Taylor dispersion experiment.

Second, the operating temperature and pressure will be restricted if commercial chromatographic equipment is used. It is not possible to state these limits precisely since a variety of equipment is available. However, one might put a broad upper limit at 700 K and $1,450 \, \text{kN} \cdot \text{m}^{-2}$. Of course, these limits could possibly be expanded by the use of special design methods.

5. CONCLUSIONS

A new tracer technique for measuring densities has been proposed and demonstrated. The technique is based on the Taylor dispersion experiment and has been proven accurate to better than 0.1%. It can possibly be improved to $\pm 0.01\%$ with proper design techniques. The method can be applied to gases or liquids, pure components or mixtures. The main limitations are that the fluids must be Newtonian or nearly so, and the

fluid must not be near its critical point. The method should be valuable as a density measurement technique alone; however, it will be of particular virtue in a program where diffusion coefficients are also being measured with the Taylor dispersion method.

ACKNOWLEDGMENT

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