TECHNICAL NOTE

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Rise of Liquid Drops in Immiscible Liquid: A Simple, Novel, and Rapid Method to Determine the Density of Microquantity Liquids

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ABSTRACT: A simple, novel, and rapid method for the determination of density of microquantity liquids is described. The method may be employed in forensic science when liquids sent for analysis are available in microquantities (even up to 0.5 μL) for which density cannot be determined either by the capillary tube method, where accurate weighing is a problem, or by the other conventional methods such as specific gravity bottle method, Pyknometer method, or the Westphal-balance method. The retrieval of the sample is also possible in this method, which allows the analyst to carry out further analysis.

KEYWORDS: forensic science, density, microquantity liquids, rise of liquid drops, immiscible liquid column

Studies on the rise of liquid drops through an immiscible liquid column have been carried out by several authors (1–28). The authors have previously dealt with the problem of rise of liquid drops with six variables, *F, D, u,* σ, η and ρ alone (*F*-drag force; *D*-diameter of the liquid drop; *u*-terminal velocity acquired by the liquid drop; η-viscosity of the liquid in the column; ρ-density of the liquid drop; σ-density of the liquid in the column) to arrive at an expression for the drag force, *F,* acting on the drop in rise through the method of dimensions. They suggested that the simple expression for the constant quantity *S* occurring in the process of simplification of the drag force expression *F* may be used to determine the density ρ of the liquid drop (1).

The expression for the density ρ obtained (1) is

$$\rho = \{(2\sigma + \lambda) - [\lambda(\lambda + 4\sigma)]^{1/2}\}/2 \quad (1)$$

where

$$\lambda = S^2\,\eta/(r/u)^3 \quad (2)$$

$$S = [(r/u)^{3/2}\,(\sigma - \rho)]/[\eta^{1/2}\,\rho^{1/2}] \quad (3)$$

r being the radius of the drop.

The physical property, density, assumes a position of great importance in the identification of pure liquids. When liquids are available in bulk quantities, conventional methods (such as specific gravity bottle, pyknometer, Westphal-balance (29–31)) may be employed to determine this physical constant. When liquids are available in small quantities and when neither the conventional methods nor the capillary tube method (where weighing is a problem) is adoptable, a new method is developed to determine the density of microquantity liquids.

Materials and Methods

A specially improvised graduated glass cylindrical tube of internal diameter 0.05 m and height 1.5 m with a small side tube attached to its bottom and sealed with a rubber septum; stop watch (Racer), accurate to 0.05 s; Hamilton precision microsyringe, accurate to 0.01 μL, and 27 liquids having considerable range of densities (Table 1) were used.

The liquids, ethylene glycol, water, chlorobenzene, and bromobenzene, which are immiscible with the corresponding drop liquids (Table 1), were selected as column liquids. Liquid drops of known volume were gently injected at the bottom of the liquid column using a graduated Hamilton Precision microsyringe. When the drop rises freely and vertically without oscillation, the terminal velocity *u* was determined by observing the time *t* required by the liquid drop of radius *r* to cover the distance *d* between two graduations on the column. All the experiments were conducted at the room temperature of 25°C.

Results and Discussion

The 27 liquid drop-liquid pair systems studied are given in Table 1. In Table 2, only ten liquid drop-liquid pairs having three data points each are presented to show that for liquid drops of different radii of a given liquid pair system, *r*/*u* is a constant. The other 17 liquid drop-liquid pair systems for which the experimental results have been obtained satisfy the same. The values of $(r/u)^{3/2}/\eta^{1/2}$, $\rho^{1/2}/(\sigma - \rho)$, and *S* are given in Table 3. The value of *S* has been found to be approximately constant for all liquid drop-liquid pair systems and its mean value is 0.313366 $m^{-1}s^2$. Table 4 furnishes the observed density of the liquids, the density of the liquids estimated from Eq 1 (using *r*/*u* and η (Table 1), *S* (mean) values),

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TABLE 1—*Liquid drop—column liquid pair systems and their physical constants.*

S1. No.	Liquid Drop	Liquid Column	ρ kgm^{-3}	σ kgm^{-3}	$(\sigma - \rho)$ kgm^{-3}	'η' Nsm^{-2}	'γ' (Nm^{-1}) $\times 10^{-3}$	r/u (s)
1.	Hexane	EG*	665.12	1108.00	442.88	0.01520	21.6	0.017192
2.	Petrol	EG*	715.38	1108.00	392.62	0.01520	16.7	0.018964
3.	Heptane	EG*	720.24	1108.00	387.76	0.01520	20.8	0.019244
4.	Naphtha	EG*	733.29	1108.00	374.71	0.01520	15.3	0.019708
5.	MIBK	EG*	792.85	1108.00	315.15	0.01520	3.1	0.022752
6.	Kerosene	EG*	797.22	1108.00	310.78	0.01520	11.9	0.022998
7.	Diesel	EG*	830.65	1108.00	277.35	0.01520	15.6	0.025111
8.	Soap oil	EG*	857.01	1108.00	250.99	0.01520	18.0	0.027218
9.	Xylene	EG*	857.50	1108.00	250.50	0.01520	13.9	0.027318
10.	Benzene	EG*	870.60	1108.00	237.40	0.01520	9.1	0.028376
11.	Palm oil	EG*	876.66	1108.00	231.34	0.01520	9.6	0.028816
12.	Groundnut oil	EG*	910.91	1108.00	197.09	0.01520	12.0	0.032461
13.	Gingely oil	EG*	915.85	1108.00	192.15	0.01520	12.3	0.033150
14.	Coconut oil	EG*	917.27	1108.00	190.73	0.01520	13.3	0.033273
15.	Castor oil	EG*	925.72	1108.00	182.28	0.01520	7.2	0.034431
16.	Sandalwood oil	EG*	960.20	1108.00	147.80	0.01520	14.1	0.040103
17.	Heptane	Water	720.37	1000.00	279.63	0.00100	38.7	0.009765
18.	Cyclohexane	Water	775.04	1000.00	224.96	0.00100	20.4	0.011578
19.	Kerosene	Water	797.34	1000.00	202.66	0.00100	43.8	0.012480
20.	Soap oil	Water	857.15	1000.00	142.85	0.00100	34.2	0.015956
21.	Xylene	Water	857.95	1000.00	142.05	0.00100	29.0	0.016010
22.	Turpentine	Water	860.03	1000.00	139.97	0.00100	41.5	0.016448
23.	Toluene	Water	860.89	1000.00	139.11	0.00100	39.7	0.016543
24.	Benzene	Water	870.78	1000.00	129.22	0.00100	35.0	0.017382
25.	Iso-amylacetate	Water	882.15	1000.00	117.85	0.00100	29.2	0.018537
26.	Water	Chlorobenzene	1000.00	1097.99	97.99	0.00071	46.1	0.019610
27.	Ethylene glycol	Bromobenzene	1108.00	1492.21	384.21	0.00085	11.2	0.008580

ρ = Density of liquid drop; σ = density of column liquid; η = viscosity of column liquid; γ = interfacial tension between liquid drop and liquid in column; r = radius of liquid drop; u = terminal velocity of drop. (r/u) = Mean experimental values.

* Ethylene glycol.

ρ, σ by specific gravity bottle; η by Ostwald viscometer; γ by the method of drops.

TABLE 2—*Experimental data for liquid drop—liquid pair systems.*

Liquid Drop-Liquid Pair Systems	Volume of Drop V (μL)	Radius of Drop r ($\times 10^{-4}$ m)	Distance Travelled d ($\times 10^{-2}$ m)	Time Taken t (secs)	Terminal Velocity u $\times 10^{-2}$ ms^{-1}	r/u (s)	Reynolds Number, R_e	Eotvos Number E_t $\times 10^{-2}$	Morton Number, M_o
Hexane in EG*	0.5	4.9237	0.4	14.0	2.8571	0.01723	2.05	19.50	1.8×10^{-5}
	1	6.2035	0.4	11.0	3.6363	0.01705	3.28	30.96	
	2	7.8159	0.4	8.8	4.5454	0.01719	5.17	49.15	
Petrol in EG*	0.5	4.9237	0.4	15.4	2.5974	0.01895	1.86	22.38	3.6×10^{-5}
	1	6.2035	0.4	12.2	3.2786	0.01892	2.96	35.53	
	2	7.8159	0.4	9.7	4.1237	0.01895	4.69	56.41	
Heptane in EG*	0.5	4.9237	0.4	15.6	2.5641	0.01920	1.84	17.73	1.8×10^{-5}
	1	6.2035	0.4	12.4	3.2258	0.01923	2.91	28.15	
	2	7.8159	0.4	9.9	4.0404	0.01934	4.60	44.69	
Naphtha in EG*	0.5	4.9237	0.4	16.0	2.5000	0.01969	1.79	23.24	4.4×10^{-5}
	1	6.2035	0.4	12.7	3.1496	0.01969	2.84	36.89	
	2	7.8159	0.4	10.1	3.9603	0.01973	4.51	58.56	
MIBK in EG*	0.5	4.9237	0.4	18.5	2.1621	0.02277	1.55	97.55	4.6×10^{-3}
	1	6.2035	0.4	14.7	2.7210	0.02279	2.46	154.86	
	2	7.8159	0.4	11.6	3.4482	0.02266	3.92	245.82	
Kerosene in EG*	0.5	4.9237	0.4	18.7	2.1390	0.02301	1.53	24.83	7.8×10^{-5}
	1	6.2035	0.4	14.8	2.7027	0.02295	2.44	39.41	
	2	7.8159	0.4	11.7	3.4188	0.02286	3.89	62.57	
Diesel in EG*	0.5	4.9237	0.4	20.4	1.9607	0.02511	1.40	16.86	3.0×10^{-5}
	1	6.2035	0.4	16.2	2.4691	0.02512	2.23	26.76	
	2	7.8159	0.4	12.8	3.1250	0.02501	3.56	42.48	
Soap oil in EG*	0.5	4.9237	0.4	22.1	1.8099	0.02720	1.29	30.25	1.8×10^{-5}
	1	6.2035	0.4	17.6	2.2727	0.02729	2.05	21.03	
	2	7.8159	0.4	13.9	2.8776	0.02716	3.27	33.39	
Xylene in EG*	0.5	4.9237	0.4	22.25	1.7976	0.02739	1.29	17.07	3.9×10^{-5}
	1	6.2035	0.4	17.50	2.2857	0.02714	2.07	27.10	
	2	7.8159	0.4	13.95	2.8674	0.02726	3.27	43.01	
Benzene in EG*	0.5	4.9237	0.4	23.1	1.7316	0.02843	1.24	24.82	1.3×10^{-4}
	1	6.2035	0.4	18.3	2.1857	0.02838	1.97	39.41	
	2	7.8159	0.4	14.5	2.7586	0.02833	3.14	62.56	

* Ethylene glycol $R_e = \sigma u D/\eta$

$E_t = g(\sigma - \rho)\, D^2/\gamma$

$M_o = g\eta^4\, (\sigma - \rho)/\sigma^2\gamma^3$

ρ, σ, η and γ from Table 1.

g 9.8 ms^{-2}; $D = 2r$.

TABLE 3—*Values of* $(\mathrm{r/u})^{1/2}/\eta^{1/2}$ and $\rho^{3/2}/(\sigma - \rho)$ and S.

S1. No.	Liquid Drop	Liquid Column	$(r/u)^{3/2}/\eta^{1/2}$	$\rho^{1/2}/(\sigma - \rho)$	S
1.	Hexane	EG*	0.018284	0.058232	0.313985
2.	Petrol	EG*	0.021182	0.068123	0.310938
3.	Heptane	EG*	0.021653	0.069211	0.312855
4.	Naphtha	EG*	0.022441	0.072267	0.310529
5.	MIBK	EG*	0.027836	0.089346	0.311553
6.	Kerosene	EG*	0.028289	0.090852	0.311375
7.	Diesel	EG*	0.032276	0.103915	0.310600
8.	Soap oil	EG*	0.036422	0.116637	0.312268
9.	Xylene	EG*	0.036623	0.116898	0.313290
10.	Benzene	EG*	0.038771	0.124287	0.311947
11.	Palm oil	EG*	0.039676	0.127986	0.310003
12.	Groundnut oil	EG*	0.047437	0.153134	0.309774
13.	Gingely oil	EG*	0.048956	0.157492	0.310848
14.	Coconut oil	EG*	0.049228	0.158792	0.310016
15.	Castor oil	EG*	0.051821	0.166917	0.310460
16.	Sandalwood oil	EG*	0.065139	0.209655	0.310696
17.	Heptane	Water	0.030515	0.095982	0.317924
18.	Cyclohexane	Water	0.039396	0.123753	0.318344
19.	Kerosene	Water	0.044088	0.139332	0.316424
20.	Soap oil	Water	0.063736	0.204950	0.310983
21.	Xylene	Water	0.064060	0.206200	0.310669
22.	Turpentine	Water	0.066707	0.209518	0.318383
23.	Toluene	Water	0.067285	0.210918	0.319010
24.	Benzene	Water	0.072469	0.228362	0.317343
25.	Iso-amylacetate	Water	0.079810	0.252024	0.316676
26.	Water	Chlorobenzene	0.103059	0.322714	0.319351
27.	Ethylene glycol	Bromobenzene	0.027260	0.086636	0.314650
				Mean	0.313366

* Ethylene glycol; (r/u), η, ρ and $(\sigma - \rho)$ from Table 1.
$S = [(r/u)^{3/2}/\eta^{1/2}]/[\rho^{1/2}/(\sigma - \rho)]$.

TABLE 4—*Comparison of density values and estimated error in percent.*

		Density, ρ, kgm^{-3}		
S1. No.	Liquid Drop	Observed*	Estimated from Eq 1	Estimated Error in %
1.	Hexane	665.12	665.77	−0.098
2.	Petrol	715.38	712.98	0.335
3.	Heptane	720.24	719.74	0.069
4.	Naphtha	733.29	730.61	0.365
5.	MIBK	792.85	791.32	0.193
6.	Kerosene	797.22	795.56	0.208
7.	Diesel	830.65	828.53	0.255
8.	Soap oil	857.01	856.24	0.090
9.	Xylene	857.50	857.44	0.007
10.	Benzene	870.60	869.65	0.109
11.	Palm oil	876.66	874.45	0.254
12.	Groundnut oil	910.91	908.85	0.226
13.	Gingely oil	915.85	914.44	0.154
14.	Coconut oil	917.27	915.41	0.203
15.	Castor oil	925.72	924.17	0.167
16.	Sandalwood oil	960.20	959.02	0.123
17.	Heptane	720.37	723.73	−0.466
18.	Cyclohexane	775.04	778.12	−0.397
19.	Kerosene	797.34	799.08	−0.218
20.	Soap oil	857.15	856.14	0.118
21.	Xylene	857.95	856.14	0.133
22.	Turpentine	860.03	862.07	−0.237
23.	Toluene	860.89	863.17	−0.265
24.	Benzene	870.78	872.29	−0.173
25.	Iso-amylacetate	882.15	883.31	−0.131
26.	Water	1000.00	1001.75	−0.175
27.	Ethylene glycol	1108.00	1109.33	−0.120

* From Table 1.

and the estimated error in percent. It may be seen from this table that the estimated and the observed density values are comparable, with an estimated error less than 0.5%. This confirms that the rising drop method may be successfully employed to determine the density of a microsample of liquid for which density cannot be determined by any other conventional method. The only unknown quantity to be determined for estimating the density of a liquid drop from Eq 1 is r/u. This may be accomplished in one or two minutes. Thus it provides a rapid means of determining the density of liquids.

The minimum amount of liquid sample required for this method is less than 1 μL and therefore it provides a solution to the analyst who prefers, as far as possible, to preserve the original microsample of a liquid for identification and confirmation through other analytical means apart from density determination.

The measurement of weight of the liquid drop is not involved in this method and hence the availability of a high-precision balance is not an essential requirement as in the case of other conventional methods, viz., specific-gravity bottle method, pyknometer method, Wesptphal-balance method (29), for establishing the accurate density value.

The added advantage of this method is that the liquid drop injected at the bottom can be retrieved from the top of the liquid column using a microsyringe or filter paper for further analysis as the drop liquid and the column liquid are immiscible.

Infrared spectrophotometry, gas-chromatography, etc., are the powerful tools used in the identification of a microsample of unknown liquid. But such sophisticated and expensive equipment is not available in many operational laboratories. At this juncture, the simple and rapid method presented here may be helpful to those who prefer to derive preliminary information about the sample through density. However, one should consider the possibility of a mixture in the unknown liquid and exercise caution in the identification of an unknown liquid based solely on density.

While working with unknown liquids, first one has to ascertain whether the liquid to be tested is immiscible with, as well as lighter than, the column liquid. This may be achieved by injecting a minimum volume of sample (approximately 0.01 μL), using a precision microsyringe, into the column liquid, thereby restricting wastage of the sample to a minimum. The authors do not suggest this method when the sample size of an unknown is a limiting factor and does not allow even a spare 0.05 μL of the sample in the process of the selection for a suitable column liquid.

Conclusion

This method may be employed to determine the density of liquids when available in small or microquantities. It may be used as a viable alternative technique in the laboratories that lack advanced instruments. The authors do not suggest that this approach is an acceptable substitute when the sample size of an unknown is a limiting factor, or for those liquids which do not have any suitable column liquid.

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