Bull. Mater. Sci., Vol. 21, No. 3, June 1998, pp. 257–261. © Indian Academy of Sciences.

Density of micro-quantity liquids by the method of rise of drops in immiscible liquids

G J SRINIVASAN*, G THIRUNAVUKKARASU† and P SATYANARAYANA†
Department of Electronics and Instrumentation, St. Peter's Engineering College, Avadi, Chennai 600 054, India
†Physics Division, Forensic Sciences Department, Chennai 600 004, India

MS received 12 January 1998; revised 18 April 1998

Abstract. The conventional methods such as specific gravity bottle method, pyknometer method, and the Westphal-balance method or the capillary tube method where accurate weighing is a problem cannot be employed when liquids are available in micro-quantities. The method described may be employed to determine the density of micro-quantity liquids (even up to $0{\cdot}5\,\mu$l) and it is found to be simple and rapid. The method also allows the analyst to retrieve the sample for further analysis.

Keywords. Density; micro-quantity liquids; rise of liquid drops; immiscible liquid column.

1. Introduction

Studies on the rise of liquid drops through an immiscible liquid column have been carried out by several authors (Klee and Treybal 1956; Saffman 1956; Bhattacharya and Venkateswarlu 1957; Houghton *et al* 1957; Harmathy 1960; Goldsmith and Mason 1962; Griffith 1962; Davis and Acrivos 1966; Zieminski and Raymond 1968; Grace *et al* 1976; Clift *et al* 1978). Srinivasan *et al* (1996) 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. It has been 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.

The expression for the density, ρ obtained (Srinivasan *et al* 1996) is

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

where

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

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

r being 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 like specific gravity bottle method, pyknometer method, Westphal-balance method etc 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 has to be developed to determine the density of the micro-quantity liquids.

In the present paper, therefore, the method and the expression for ρ suggested earlier (Srinivasan *et al* 1996) have been employed to determine the density, ρ of liquid drops and the results obtained have been presented.

2. Experimental

2.1 *Equipment and liquids used*

A long graduated glass cylinder (of internal diam. 0·05 m and height 1·5 m) with a small side tube attached to it at the bottom and sealed with a rubber septum (figure 1); stop watch (Racer), accurate to 0·05 sec; Hamilton precision syringe, accurate to 0·01 μl; Ethylene glycol and soap oil (Ranbaxy purified grade); Hexane, Heptane, MIBK, Xylene, Cyclohexane, Benzene, Toluene, Iso-amyl acetate (Fisher purified grade); Turpentine (Chemlab purified grade); Water, Petrol, Kerosene, Naphtha and Diesel (distilled); Palm oil, Groundnut oil and Gingely oil (KKR refined grade); Coconut oil (VVD refined grade); Castor oil (Richardson refined grade); Sandalwood oil (Vibhav purified grade), were used (table 2).

---

*Author for correspondence

2.2 *Method*

The liquids viz. ethylene glycol, water, chlorobenzene and bromobenzene, which were immiscible with the corresponding drop liquids (table 2) were selected as column liquids and used for filling the cylindrical column. Liquid drops of known volume were gently injected at the bottom of the liquid column using a graduated Hamilton Precision micro-syringe. When the drop rised 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. Assuming the rising drop to be a sphere of volume, V of diameter, D then the drop radius was obtained from $r = (3V/4\pi)^{1/3}$, where $r = D/2$. All the experiments were conducted at room temperature (25°C).

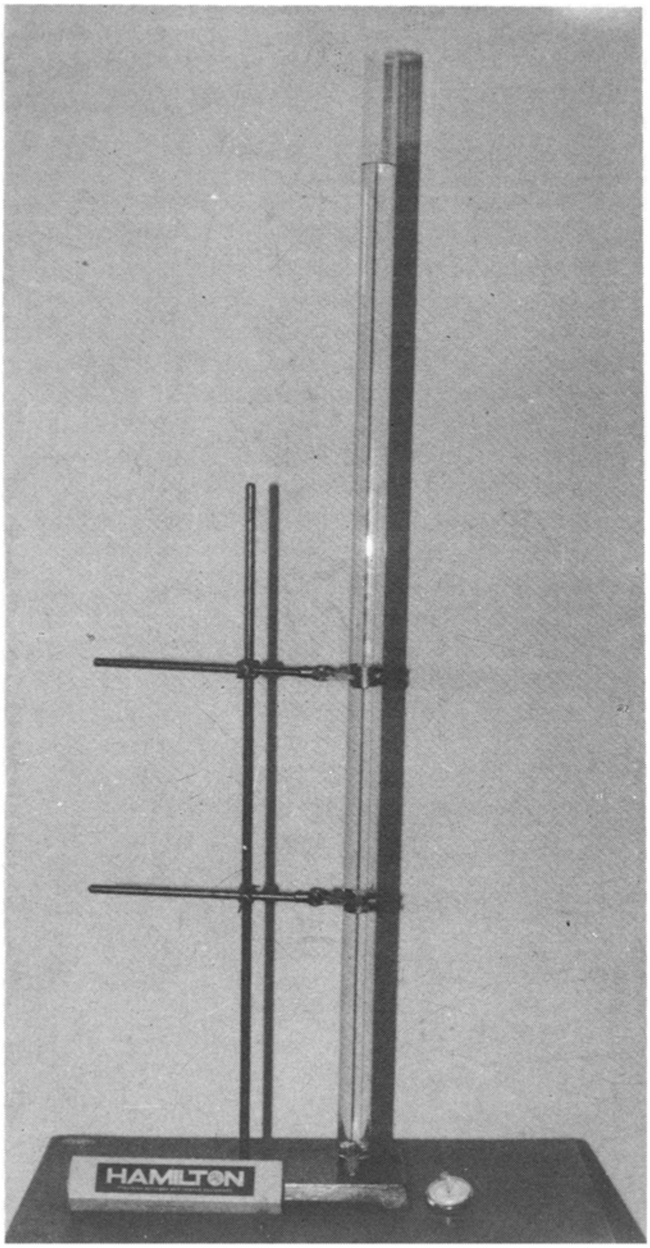

Figure 1. The set up used for conducting rising drop experiments.

3. Results and discussion

The data presented in table 1 for ten liquid drop–liquid pair systems having three data points each shows that r/u is approximately constant. The other seventeen liquid drop–liquid pair systems (table 2) for which the experimental results have been obtained satisfy the same. The density of the column liquids and the drop liquids, viscosity of the column liquids, interfacial tension between the liquid drop and liquid column given in table 2 were determined by the specific gravity bottle method, Ostwald Viscometer and the method of drops, respectively. The values of $(r/u)^{3/2}/\eta^{1/2}$, $\rho^{1/2}/(\sigma - \rho)$, and S are given in table 3. Table 4 furnishes the observed density of the liquids (refer table 2) and the density of liquids determined from (1) and the estimated error in percentage. It may be seen from table 1 that for liquid drops of different radii of a given liquid pair system, r/u is a constant. The value of S calculated from (3) has been found to be approximately constant for all the liquid drop–liquid pair systems (table 3) and its mean value is $0{\cdot}313366\ \mathrm{m^{-1}\,s^2}$ (table 3). This mean value of S is also found to be approximately equal and agree to the experimental mean value of S ($0{\cdot}3176\ \mathrm{m^{-1}\,s^2}$) predicted previously for the thirteen liquid drop–liquid pair systems (Srinivasan *et al* 1996). The density values of the liquid drop estimated from (1) (column 4, table 4) using the experimental mean value of S ($0{\cdot}313366\ \mathrm{m^{-1}\,s^2}$; table 3), r/u (table 2) and η (table 2) show that they are comparable with the observed density value of the liquids determined by the specific gravity bottle method (column 3, table 4). The estimated error in percentage (column 5, table 4) is found to be less than 0·5% between the observed and the calculated density values (table 4).

Since by knowing the radius, r of the liquid drop and the terminal velocity, u attained by it in the liquid column, one may determine the density of the liquid drop from (1) with the experimentally predicted mean value of S ($0{\cdot}313366\ \mathrm{m^{-1}\,s^2}$, table 3) and the viscosity of the liquid in the column (table 2), the only unknown quantity to be determined being r/u. This may be accomplished in one or two min.

The minimum amount of liquid sample required for this method is less than 1 μl, and therefore this method may be adopted to determine the density of a liquid sample available in small or micro-quantities for which the density cannot be determined by any other conventional method. It also provides a solution to the analyst who prefers, as far as possible to preserve the original

Table 1. Experimental data for liquid drop–liquid pair systems.

Liquid drop–liquid pair systems	V (μl)	r ($\times 10^{-4}$ m)	d ($\times 10^{-2}$ m)	t (sec)	u ($\times 10^{-2}$) (m s^{-1})	r/u (s)	Reynolds number (R_e)	Eotvos number E_t ($\times 10^{-2}$)	Morton number (M_0)
Hexane	0·5	4·9237	0·4	14·0	2·8571	0·01723	2·05	19·50	$1{\cdot}8\times 10^{-5}$
in EG*	1·0	6·2035	0·4	11·0	3·6363	0·01705	3·28	30·96	
	2·0	7·8159	0·4	8·8	4·5454	0·01719	5·17	49·15	
Petrol	0·5	4·9237	0·4	15·4	2·5974	0·01895	1·86	22·38	$3{\cdot}6\times 10^{-5}$
in EG*	1·0	6·2035	0·4	12·2	3·2786	0·01892	2·96	35·53	
	2·0	7·8159	0·4	9·7	4·1237	0·01895	4·69	56·41	
Heptane	0·5	4·9237	0·4	15·6	2·5641	0·01920	1·84	17·73	$1{\cdot}8\times 10^{-5}$
in EG*	1·0	6·2035	0·4	12·4	3·2258	0·01923	2·91	28·15	
	2·0	7·8159	0·4	9·9	4·0404	0·01934	4·60	44·69	
Naphtha	0·5	4·9237	0·4	16·0	2·5000	0·01969	1·79	23·24	$4{\cdot}4\times 10^{-5}$
in EG*	1·0	6·2035	0·4	12·7	3·1496	0·01969	2·84	36·89	
	2·0	7·8159	0·4	10·1	3·9603	0·01973	4·51	58·56	
MIBK	0·5	4·9237	0·4	18·5	2·1621	0·02277	1·55	97·55	$4{\cdot}6\times 10^{-3}$
in EG*	1·0	6·2035	0·4	14·7	2·7210	0·02279	2·46	154·86	
	2·0	7·8159	0·4	11·6	3·4482	0·02266	3·92	245·82	
Kerosene	0·5	4·9237	0·4	18·7	2·1390	0·02301	1·53	24·83	$7{\cdot}8\times 10^{-5}$
in EG*	1·0	6·2035	0·4	14·8	2·7027	0·02295	2·44	39·41	
	2·0	7·8159	0·4	11·7	3·4188	0·02286	3·89	62·57	
Diesel	0·5	4·9237	0·4	20·4	1·9607	0·02511	1·40	16·86	$3{\cdot}0\times 10^{-5}$
in EG*	1·0	6·2035	0·4	16·2	2·4691	0·02512	2·23	26·76	
	2·0	7·8159	0·4	12·8	3·1250	0·02501	3·56	42·48	
Soap oil	0·5	4·9237	0·4	22·1	1·8099	0·02720	1·29	30·25	$1{\cdot}8\times 10^{-5}$
in EG*	1·0	6·2035	0·4	17·6	2·2727	0·02729	2·05	21·03	
	2·0	7·8159	0·4	13·9	2·8776	0·02716	3·27	33·39	
Xylene	0·5	4·9237	0·4	22·25	1·7976	0·02739	1·29	17·07	$3{\cdot}9\times 10^{-5}$
in EG*	1·0	6·2035	0·4	17·50	2·2857	0·02714	2·07	27·10	
	2·0	7·8159	0·4	13·95	2·8674	0·02726	3·27	43·01	
Benzene	0·5	4·9237	0·4	23·1	1·7316	0·02843	1·24	24·82	$1{\cdot}3\times 10^{-4}$
in EG*	1·0	6·2035	0·4	18·3	2·1857	0·02838	1·97	39·41	
	2·0	7·8159	0·4	14·5	2·7586	0·02833	3·14	62·56	

*Ethylene glycol.

$R_e = \sigma u D/\eta$; $E_t = g(\sigma-\rho)D^2/\gamma$; $M_0 = g\eta^4(\sigma-\rho)/\sigma^2\gamma^3$.

ρ, σ, η and γ from table 2; $g = 9{\cdot}8$ m s^{-2}; $D = 2r$.

Table 2. Liquid drop–column liquid pair systems and their physical constants.

Sl. no.	Liquid drop	Liquid column	ρ (kg^{-3})	σ (kg^{-3})	$(\sigma-\rho)$ (kg^{-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 the liquid drop; σ, density of the column liquid; η, viscosity of the column liquid; γ, interfacial tension between the liquid drop and the liquid in the column; r, radius of the liquid drop; u, terminal velocity of the drop.
(r/u): Mean experimental values. *Ethylene glycol.

Table 3. The values of $(r/u)^{3/2}/\eta^{1/2}$ and $\rho^{1/2}/(\sigma-\rho)$ and S.

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

Table 4. Comparison of density values and estimated error in percentage.

Sl. no.	Liquid drop	Density ρ (kg^{-3}) Observed*	Estimated from (1)	Estimated error (%)
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 2.

liquid samples in small quantities for identification and confirmation through other analytical means apart from density determination.

Since the measurement of weight of the liquid drop is not involved in this method, 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, Westphal-balance method (Serence *et al* 1970; O'Hara and Osterburg 1974; Giancoli 1984) etc for getting the accurate density value, and hence this method may be employed in any operational laboratory where high precision and expensive equipment is not available for accurate weighing.

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 micro-syringe or filter paper for further analysis as the drop liquid and the column liquid are immiscible.

4. Conclusion

This method may be employed to determine the density of liquids available in small or micro-quantities and also provides a practical alternative to other conventional methods. The authors do not suggest that this approach is an acceptable substitute for those liquids which do not have any suitable column liquid. Therefore, the column liquid should be selected in such a way that it is immiscible with as well as denser than the liquid to be tested.

References

Bhattacharya S P and Venkateswarlu D 1957 *Trans. Indian Inst. Chem. Engrs.* **10** 25

Clift R, Grace J R and Weber M E 1978 *Bubbles, drops and particles* (New York: Academic Press)

Davis R E and Acrivos A 1966 *Chem. Eng. Sci.* **26** 681

Giancoli D C 1984 *General physics* (New Jersey: Prentice Hall Inc)

Goldsmith H L and Mason S G 1962 *J. Fluid. Mech.* **14** 42

Grace J R, Wairegi T and Nguyen T H 1976 *Trans. Inst. Chem. Eng.* **54** 167

Griffith R M 1962 *Chem. Eng. Sci.* **17** 1057

Harmathy T Z 1960 *Aiche. J.* **6** 281

Houghton G, Ritchie P D and Thomson J A 1957 *Chem. Eng. Sci.* **7** 111

Klee A J and Treybal R E 1956 *Aiche. J.* **2** 444

O'Hara C E and Osterburg I W 1974 *An introduction to criminalistics* (London: Indiana University Press)

Saffman P G 1956 *J. Fluid Mech.* **1** 249

Serence Jr M, Lemon H B and Stephenson R J 1970 *Analytical experimental physics* (London: The University of Chicago Press)

Srinivasan G J, Satyanarayana P and Thirunavukkarasu G 1996 *Curr. Sci.* **71** 989

Zieminski S A and Raymond D R 1968 *Chem. Eng. Sci.* **23** 17